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**TITLE**

THE ROLE OF LATTICE VIBRATIONS IN THE ZERO  
FIELD SPLITTING OF Gd<sup>3</sup> IN AN ETHYLSULPHATE  
HOST LATTICE

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The Role of Lattice Vibrations in the Zero Field Splitting  
of  $Gd^{3+}$  in an Ethylsulphate Host Lattice

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A thesis submitted for the degree of Doctor of Philosophy.

University of Warwick  
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April 1993.

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## DECLARATION

This thesis is submitted to the University of Warwick in support of my application for admission to the degree of Doctor of Philosophy. It contains an account of my work carried out in the Department of Physics at the University of Warwick in the period October 1989 to April 1993 under the supervision of Dr. J M Dixon. The work described is the result of my own independent research, except where specifically acknowledged in the text. No part of this thesis has been submitted in respect of a degree to this or any other University.

## SUMMARY

The crystal field theory of B-state ions is characterised by the need to use high order perturbation theory in order to get non-zero contributions to the zero field splitting. As a consequence, the splitting is usually a delicate balance between several competing mechanisms. A typical example is the splitting of the  $^8S_{7/2}$  ground state of  $Gd^{3+}$  ions in lanthanum ethylsulphate (GdES), and over the years a great deal of effort has been expended in trying to get agreement with experimental data. The result of these efforts is a theoretical splitting which is around 20% greater than the experimental splittings. In addition, they suggest that the splitting is independent of temperature, yet it is well known that the splitting exhibits a particularly interesting temperature dependence. The reason for this is that the existing mechanisms are calculated on the assumption that the lattice is stationary, and of course this is unrealistic, even at absolute zero.

In this thesis, our intention is to investigate the effect of inserting lattice vibrations into the GdES crystal lattice. In particular, we examine how much one of the most important inter-site mechanisms is changed under these circumstances. To do this we use a many-electron theory, due to Stevens, which allows effective crystal field operators (and in particular spin correlated crystal field operators) to be calculated in a simple way. Although this theory was originally developed for use in a stationary lattice, the modifications required to incorporate lattice vibrations are comparatively straightforward. The method has the drawback that it leads to a complicated formalism, and so we are forced to make certain approximations in order to make the problem tractable. Within the framework of these approximations we find that the introduction of lattice vibrations causes a negative temperature dependent contribution to be added to the inter-site mechanism. The new contribution is of the right sign and order of magnitude to improve agreement with experiment, but the actual temperature dependence is incorrect in the low temperature limit. We also examine some of the other mechanisms which could lead to an improvement in the theoretical temperature dependence, in particular those related to the thermal expansion of the lattice.

## INTRODUCTION

The idea that the energy levels of a paramagnetic ion are modified in a crystalline environment is not a new one. As long ago as 1929, Becquerel realised that such an ion would experience an electric field due to the neighbouring ligands, and in the same year Bethe showed that this electric field would split the free ion levels in a manner characteristic of the point group symmetry of the crystal lattice [Becquerel 1929; Bethe 1929]. In the following year, Kramers showed that if the ion possessed an odd number of magnetic electrons, the new energy levels would be at least doubly degenerate. This is known as Kramers' theorem (Kramers, 1930). The study of the splitting of energy levels under the influence of a crystalline electric field, using the techniques developed by these authors, is known as Crystal Field Theory.

The philosophy behind Crystal Field Theory is quite simple: one writes down the potential energy of the magnetic electrons in the crystal field, and then one uses degenerate first order perturbation theory to calculate how the free ion levels are split (Hutchings 1964). However, one pays a price for this simplicity. The simple crystal field model cannot be used to make accurate *ab initio* estimates of splittings, because the magnetic electrons undergo other more complex interactions with the lattice, as well as a purely electrostatic interaction with the neighbouring ligands. Instead, one usually considers the various terms in the crystal field potential to be multiplied by a set of free parameters (often called 'crystal field parameters'), and with the help of the Crystal Field Theory, these are fitted to experimental data. The free parameters then incorporate the effect of all interactions (Low 1960). In fact, the term Crystal Field Theory is a bit of a misnomer, because the origin of crystal field splittings often has little to do with the electrostatic crystal field! The splittings observed in the rare-earths are an example of this. The success of this approach relies on the fact that the perturbation due to other mechanisms can be written as an effective potential with the same symmetry as the electrostatic crystal field (Newman 1971). Theories which attempt to model crystal field splittings in a more fundamental way, in particular

by allowing for the many-body aspects of the problem, are called Molecular Orbital Theories [Zeiger and Pratt 1973].

Most of the work in crystal field theory has focused on the splitting of the ground state of an ion, because these splittings are the easiest to measure experimentally. If the ground state of the free ion possesses some orbital degeneracy, then the parametrisation procedure mentioned above provides a quite satisfactory description of the splitting in a crystalline environment, even though the splittings observed are often due to a combination of many interactions within the crystal. However, in the absence of orbital degeneracy in the ground state, the parametrisation procedure fails altogether. This is because any degeneracy in the ground state is due to the resultant spin of the magnetic electrons, and a crystal field cannot resolve any spin degeneracy by itself (i.e. in first order perturbation theory). Therefore one must have recourse either to higher order perturbation theory, involving crystal fields and operators involving electron spins, or some sort of molecular orbital theory. The need to use higher order perturbation theory would seem to be reflected in the relative magnitude of the splittings observed in S-state ions. For instance, in the rare-earths, crystal field splittings are of the order of  $100 \text{ cm}^{-1}$  for orbitally degenerate ground states, but they are only of the order of  $0.1 \text{ cm}^{-1}$  for orbital singlet ground states [Abragam and Bleaney 1970]. The mechanisms responsible for the splitting of an orbital singlet are therefore comparatively weak and are of little importance in the theory of orbitally degenerate ground states.

In this thesis, we will be concerned with the splitting of the ground state of the  $\text{Gd}^{3+}$  ion in an ethylsulphate host lattice. Gadolinium is a member of the rare-earth series, and the  $\text{Gd}^{3+}$  ion has the electronic configuration  $4f^7$ , which means that the ground state of the free ion is an orbital singlet. However, the resultant spin is equal to  $7/2$ , and so the ground state has an eightfold degeneracy. In the ethylsulphate lattice, this degeneracy is resolved into four doublets. For about thirty years now, physicists have been trying to account for the magnitude of this splitting. In CHAPTER 1 we will examine some of the ideas and mechanisms which have been considered in the past, and we will see that, by them-

seives, they provide a wholly inadequate theoretical picture. Also in this chapter we will examine the properties of the energy levels of a free  $Gd^{3+}$  ion, and we will also look at the failure of the 'conventional' crystal field theory for  $Gd^{3+}$ . Given the conclusions of chapter 1, we soon realise that a more sophisticated approach is called for. This was provided by K.W.H Stevens, who developed a systematic procedure for dealing with magnetic phenomena in insulating crystals. Although Stevens' theory was originally designed with a view to investigating exchange interactions, it can also be used to investigate crystal field phenomena. We will discuss this in CHAPTER 2. In this chapter we will also discuss a concept which is of the greatest importance in the crystal field theory of S-state ions, namely the Spin correlated crystal field (SCCF).

The total splitting of the ground state of  $Gd^{3+}$  in the ethylsulphate host results from a combination of many different mechanisms, most of which make the assumption that the magnetic 4f-electrons remain localised on the central ion. But it had been thought that the discrepancy between theory and experiment could be explained by considering mechanisms in which a 4f-electron is excited into an orbital on one of the neighbouring ligands, and then back down to the central ion. This idea has been investigated by Christodoulos et al. (Christodoulos et al. 1966), using the SCCF and Stevens' theory. This mechanism, when added to the others, gives a value for the splitting which is very close to that which is observed experimentally (Tuszynski and Dixon 1967). We will examine this mechanism in detail in CHAPTER 3.

Although Christodoulos' mechanism gives close agreement with experiment, when added to the other existing mechanisms, it is not perfect. One reason is thought to be that all of the existing mechanisms have been calculated on the assumption that the lattice is stationary, a situation which is of course never realised in practice. The rest of the thesis will be dedicated to the estimation of the contribution which lattice vibrations make to the splitting of the ground state. In doing this we will make use of Stevens' theory, albeit in a slightly modified form. The modifications which have to be made will be discussed in CHAPTER 4. In this chapter we will also briefly discuss in more general terms the role which lattice



vibrations play in ligand field phenomena. For instance, if the ground state is orbitally degenerate, lattice vibrations can induce far more fundamental effects than a simple change in the magnitude of the crystal field splitting.

From chapter 5 onwards, we will be concerned with the calculation of our mechanism. We will do this by estimating how much Christodoulos' mechanism is changed when lattice vibrations are introduced. As we mentioned earlier, the BCCP plays a vital role in calculating splittings in  $M$ -state ions. Stevens' method allows us to calculate the size of the BCCP in a simple way, and from this we can obtain the contribution which a given mechanism makes to the zero field splitting. In CHAPTER 5, we will discuss the formulation of the problem. To do this, we will need to know the many-electron Hamiltonian for the electrons and nuclei in the lattice. After writing this down, we will use the techniques described in chapters 2,3 and 4 to arrive at an expression for the magnitude of the contribution which our mechanism makes to the BCCP. In order to make the calculation tractable, it will be necessary to make some assumptions along the way. We will describe and attempt to justify these assumptions. By the end of the chapter it will be clear that we are left with a rather lengthy expression to evaluate, even if we restrict ourselves to the harmonic approximation for the lattice vibrations.

Since our mechanism depends on the vibrations of the lattice, the expression derived in chapter 5 will be a function of the displacements of the ligands in the lattice. This is not the most convenient formalism with which to work, so in CHAPTER 6 we will address the problem of converting the ligand displacements to temperature dependent factors. To do this, we will first of all rewrite the ligand displacements in terms of the normal coordinates of the lattice, and then the normal coordinates will be rewritten in terms of phonon annihilators and creators. The temperature dependence then emerges on performing a thermal average over all of the lattice modes. In chapter 6 we will also discuss the model which is used to calculate the normal coordinates, since several simplifications have had to be made, owing to the complex structure of the ethylsulphate lattice. We have therefore restricted ourselves to a treatment in which we

consider only the local modes of the  $Gd^{3+}$  ion and its nearest neighbours. We will however discuss the various models which incorporate all of the modes of the lattice. The subject of CHAPTER 7 will be the actual calculation of these normal coordinates. In doing this we will make full use of the techniques of group theory, in order to effect a reduction of the force and mass matrices to block diagonal form. Although modern computational techniques make this procedure unnecessary, the author feels that the use of the group theory leads to a more elegant solution of the problem. In this chapter we will also discuss the choice of force constants, because, to the best of our knowledge, no structural data of this nature exists for GdES. The models which incorporate all of the modes of the lattice prove to be invaluable in this regard.

Having completed the calculation of the lattice vibrations, we turn our attention to the electronic part of the calculation in CHAPTER 8. As was hinted earlier, this involves the calculation of a rather complicated expression. We begin the chapter by discussing the choice of analytical wavefunctions which we used, and then we will discuss some of the approximations which can be made to ease the numerical calculations. Finally we will examine the algebraic techniques required to evaluate the various one and two-body matrix elements which appear in the final expression.

In the final chapter we will present our final results, along with the various radial integrals needed to evaluate the matrix elements. The presentation is complicated slightly by the fact that there is a slight ambiguity in the choice of force constants in chapter seven, but nevertheless we can still draw some definite conclusions from the results. These will be discussed in detail in the final concluding chapter. In this concluding chapter we will also examine some of the additional mechanisms which could play a role in the splitting. In particular, we will examine the effects of lattice anharmonicity, via the linear expansion of the lattice with temperature.

## CHAPTER ONE

### Crystal Field Theory of the Rare Earths

#### 1.1 Introduction

When a paramagnetic ion becomes part of a crystal lattice, its properties are often modified quite considerably. The precise nature of these changes depends on which ion is being considered and in which host it is embedded. Consider, for instance, a potassium atom. It is paramagnetic by virtue of having a single outer  $4s$ -electron, and when it becomes part of a potassium crystal, it loses its outer  $4s$ -electron, which then becomes part of a sea of conduction electrons. The paramagnetic properties of the system are then best described using the band theory of electrons [Zeiger and Pratt 1973]. On the other hand, when a rare earth ion is present in dilute concentration in an insulating crystal lattice, the result is a splitting (perturbation) of the free ion energy levels, with the paramagnetic electrons (in this case the  $4f$ -electrons) remaining localised on the rare-earth ion. In this thesis we will be solely concerned with this latter type of behaviour. In this chapter we will review the properties of the rare-earths, and we will also examine how one normally tackles the problem of calculating the splitting of rare-earth energy levels in a crystal. We will be specifically concerned with a  $Gd^{3+}$  ion in an ethylenephosphate host lattice.

#### 1.2 The Rare Earths

The rare-earths constitute a group of 13 elements in the periodic table, with atomic numbers ranging from  $Z=58$  to  $Z=70$ . They are characterised by having an incomplete shell of  $4f$ -electrons in the triply ionised state. Although the triply ionised state is the most common one, others (e.g.  $2+$  and  $4+$ ) are possible, especially if this results in either an empty, completely filled, or half-filled  $4f$  shell. The series starts at  $Z=58$  with cerium, the  $Ca^{3+}$  ion having just one  $4f$ -electron, and ends at  $Z=70$  with ytterbium, the  $Yb^{3+}$  ion having thirteen  $4f$ -electrons. Sometimes, lanthanum ( $Z=57$ ) and lutetium ( $Z=71$ ) are classed as rare-earths, even though they

have empty and completely filled 4f shells respectively. An extensive account of the physical and chemical properties of the rare-earths may be found in the book by Deane and Spedding (1961).

Since our interest lies in the properties of a gadolinium compound, we will use gadolinium to illustrate some further properties of the rare-earths. Neutral gadolinium has seven 4f-electrons, and the ground state electronic configuration is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$  (which from now on we will abbreviate to  $4f^7 5s^2 5p^6 5d^1 6s^2$  for simplicity). In moving to the triply ionised state, the gadolinium atom loses the 5d and 6s electrons, so that the  $Gd^{3+}$  ion has the configuration  $4f^7 5s^2 5p^6$ . Freeman and Watson (1962) have shown that for a  $Gd^{3+}$  ion (a  $Gd^{2+}$  ion with both 6s-electrons present), the 4f charge density peaks at about 0.6 Å, whereas the 5s and 5p charge densities peak at about 1.2 Å. These charge densities are illustrated in figure 1.1. The 4f-electrons are thus fairly well localised within the ion. It should be noted that although these results were obtained for gadolinium, the conclusions hold qualitatively for all of the rare-earths. The localised nature of the 4f-electrons has important consequences for the crystal field theory of the rare-earths. This is because the outer 5s- and 5p-electrons tend to shield the 4f-electrons from the full effects of the crystal field. It was thought initially that this was due to a screening effect (Freeman and Watson 1964), but it is now thought that the outer electrons simply prevent the neighbouring ligands from approaching as close as they would in the absence of the outer electrons (Abragam and Blaney 1970). This situation should be contrasted with that of the transition ions, where it is the 3d shell which is incomplete. For these ions, there is very little shielding, because the 3d shell is the outermost shell. As a consequence, the crystal field interaction is fairly strong in the transition ions ( $\sim 10000\text{ cm}^{-1}$ ), whereas in the rare-earths it is comparatively weak ( $\sim 100\text{ cm}^{-1}$ ) (Abragam and Blaney 1970). For this reason, the crystal field theory of the transition ions is somewhat different from that of the rare-earths.

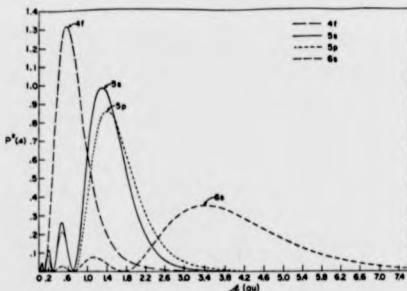


Figure 1.1. Radial probability functions for the outer electrons on a  $Gd^{3+}$  ion (from Freeman and Watson (1962)). Note how the 4f-electrons are tightly bound within the ion.



Figure 1.2. Observed level structures of the RE ions (from Dieke (1968)). The energy scale is in units of  $10^3 \text{ cm}^{-1}$ . A semicircle on a level indicates that it fluoresces in  $LaCl_3$ . The thickness of a level indicates the crystal field splitting of the level in  $LaCl_3$ .

### 1.3 Rare Earth Energy Levels

Before we examine the crystal field theory of the rare earths in insulating hosts, we must first examine in detail the energy levels of the free ions. The theoretical techniques for doing this have been known for many years [Slater 1929; Racah 1942a,b, 1943, 1949], and excellent contemporary accounts of these works can be found in the books by Bransden and Joachain (1983), Zeiger and Pratt (1973) and Condon and Odabasi (1980). The usual starting point is the following many-electron Hamiltonian for the free ion:

$$H = H_{\text{kin}} + H_{\text{ee}} + H_{\text{so}} \quad (1.1)$$

In this expression,  $H_{\text{kin}}$  represents the electron kinetic energy and potential energy in the electric field of the nucleus,  $H_{\text{ee}}$  is the electrostatic interaction between the electrons, and  $H_{\text{so}}$  is the spin-orbit coupling. It is usual to ignore the smaller interactions (e.g. hyperfine interaction) in a first treatment [Dieke 1968]. An exact solution of this Hamiltonian is not possible, and so a perturbative treatment is necessary. The unperturbed Hamiltonian  $H_0$  is usually taken to be [Bransden and Joachain 1983]

$$H_0 = H_{\text{kin}} + \sum_i V(r_i) \quad (1.2)$$

where  $V(r_i)$  is the average potential felt by the  $i^{\text{th}}$  electron due to the motion of the other electrons. The eigenstates of  $H_0$  are products of one-electron orbitals. When these products are antisymmetrised in accordance with the Pauli principle, the eigenfunctions become:

$$\Psi = (N!)^{-1/2} \sum_P (-1)^P P \{ U_{\alpha}(q_1) U_{\beta}(q_2) \dots U_{\gamma}(q_N) \} \quad (1.3)$$

Here  $N$  is a normalisation factor,  $P$  is the permutation operator,  $\alpha, \beta, \dots$  are the set of quantum numbers  $(n, l, m, m_s)$  for the orbitals  $U_{\alpha}, U_{\beta}, \dots$  and the  $q_i$  represent the space and spin variables of the  $i^{\text{th}}$  electron. The energy of the state  $\Psi$  is equal to the sum of the individual energies  $E_{\alpha}, E_{\beta}, \dots$  of the orbitals  $U$ . These energies are independent of the  $m_l$  and  $m_s$ , and so the state  $\Psi$  is highly degenerate. All states  $\Psi$  which have the

same energy are collectively referred to as a 'configuration'. A configuration is specified by the set of pairs of quantum numbers  $(n_i, l_i)$  which are present in  $\Psi$ , and this gives rise to the familiar  $1s^2 2s^2 \dots$  notation. In a rare-earth atom, different configurations are separated by energies of around  $10^4 \text{ cm}^{-1}$ , and so in a first approximation the 'configuration interaction' may be ignored [Dieke 1968].

The other terms in  $H$  may now be treated as a perturbation on  $H_{ee}$ . The way in which one goes about this depends on the relative strengths of  $H_{ee}$  and  $H_{so}$ . One has two limiting cases: if  $H_{ee} \gg H_{so}$ , one has a situation known as LS-coupling, and if  $H_{so} \gg H_{ee}$ , then one has jj-coupling. Both cases are treated in most textbooks on quantum mechanics e.g. [Branadan and Joachain 1983; Liboff 1985]. Unfortunately, the rare-earth ions are not treated adequately by either case, but they are "close" to LS-coupling behaviour [Abragam and Bleaney 1970]. The true situation is known as intermediate coupling, and its consequences may be derived from the LS-coupling case.

In the LS-coupling case, one first considers the effect of the interaction between the electrons on the unperturbed configurations. The degeneracy of a configuration results from the fact that the unperturbed Hamiltonian  $H_e$  is invariant under separate rotations of the electron coordinates  $x_i, y_i$  and  $z_i$  [Heine p76]. When  $H_{ee}$  is included, this invariance is lost, but the new Hamiltonian is invariant under simultaneous rotations of all the electron coordinates. The effect of this loss of symmetry is to split a configuration up into a series of 'terms' of well defined total orbital angular momentum  $L$ . These terms also have a well defined spin  $S$ , and so they possess a  $(2L+1)(2S+1)$ -fold degeneracy, each energy level being characterised by different values of  $M_L$  and  $M_S$  [Heine 1960; Branadan and Joachain 1983, p341]. Terms are normally denoted by the notation  $2S+1L$ . Note that any completely filled shells in a configuration do not contribute to the term structure [Branadan and Joachain 1983 p342]. The actual energies of the terms are calculated in terms of the Slater integrals [Dieke 1968; Condon and Odabasi 1980]. The energy gap between terms in the rare-earths is of the order of  $10^4 \text{ cm}^{-1}$  [Orton 1988].

Once the term structure has been obtained, the spin-orbit interaction can be included. Again this can be visualised in terms of the symmetry properties of the Hamiltonian [Heine p85], and the effect is to split the terms up into 'levels', characterised by a well defined total angular momentum  $J$ , giving  $(2J+1)$ -fold degenerate levels [Bransden and Joachain p346]. Since a filled shell in a configuration contributes nothing to the term structure, the level scheme is determined purely by the incomplete shells in the configuration. In the rare-earths, level splittings are of the order of  $10^3 \text{ cm}^{-1}$  [Orton 1968].

In the rare-earths, the calculation of the complete level structure can be quite a daunting task, as an inspection of figure 1.2 will show. However in crystal field theory, we are usually only interested in the ground level and the first few excited levels. In LS-coupling, there is a simple set of rules, called Hund's rules, which allow us to find  $L$ ,  $S$  and  $J$  for the ground level [Zeiger and Pratt p74]. Our interest lies in  $\text{Gd}^{3+}$ , and so we will consider this as an example. Hund's rules are:

- 1: Find the maximum value of  $S$  (= maximum value of  $\sum m_s$ ) for the configuration under consideration.
- 2: For this value of  $S$ , find the maximum value of  $L$  (= maximum value of  $\sum m_l$ ) for the configuration.
- 3: If the shell is less than half full,  $J = |L-S|$ .
- 4: If the shell is more than half full,  $J = |L+S|$ .

The configuration of  $\text{Gd}^{3+}$  is  $4f^7$ , and so Hund's rules tell us that  $S=7/2$ ,  $L=0$ , and so  $J=7/2$ . The LS-coupling ground level therefore has an eight-fold degeneracy, and is written in spectroscopic notation as  $^8S_{7/2}$ . The absence of orbital angular momentum in the ground level is a characteristic property of half-filled shells, in the LS-coupling approximation.

As we mentioned earlier, the LS-coupling scheme is only partially successful in the rare-earths. Instead, they are most correctly described using the intermediate coupling scheme. To see what effect this has, let us consider for a moment the LS-coupling scheme. It is based on the assumption that the spin-orbit interaction is much smaller than the electron-electron



interaction in the atom of interest. When this is the case it is reasonable to assume that  $H_{so}$  only has matrix elements which are diagonal in  $L$  and  $S$ . That is, in LS-coupling we do not get any mixing of terms. This fact then allows us to define an effective spin-orbit operator for a given term by making the following replacement (Zeiger and Pratt p80)

$$H_{so} = \sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i \rightarrow \lambda \mathbf{L} \cdot \mathbf{S} \quad (1.4)$$

$\mathbf{L}$  and  $\mathbf{S}$  are the total orbital and spin angular momenta for the term, and  $\lambda$  is given in equation (3.56) of Zeiger and Pratt. This formula then leads to all of the well known consequences of LS-coupling (e.g. the Lande interval rule) (Zeiger and Pratt 1973). In the intermediate coupling regime,  $H_{so}$  is not necessarily small compared with  $H_{ee}$ , and so the off-diagonal matrix elements of  $H_{so}$  are no longer negligible. Now term mixing can occur. Therefore the levels no longer originate from just one term of given  $L$  and  $S$ , but also from other terms with different  $L$  and  $S$ . However, they must combine to give the same  $J$  and  $M_J$ , because  $H_{so}$  commutes with  $J$  and  $J_z$  (Zeiger and Pratt p82). The mathematical procedure for finding the intermediate coupling ground state wavefunctions involves the simultaneous diagonalisation of  $H_{ee}$  and  $H_{so}$ , details of which can be found in Dieke (1968). The calculation has been performed by Wybourne for the ground state of  $Gd^{3+}$  (Wybourne 1968). He gives

$$|^8S_{7/2}\rangle = 0.987|^8S_{7/2}\rangle + 0.162|^6P_{7/2}\rangle - 0.018|^6D_{7/2}\rangle + \dots \quad (1.5)$$

Where .... refers to smaller admixtures from higher terms. So we see that although the ground state is made up predominantly from the LS-coupling ground state  $^8S_{7/2}$ , we have to include a non-negligible contribution from a higher  $^6P$  ( $L=5/2$ ,  $S=1$ ) term. Ignoring these extra terms can lead to errors of up to 10% in calculated quantities (Judd and Lindgren 1961).

#### 1.4 The Point Charge Approximation

Now that we have found out about the first few energy levels of the  $Gd^{3+}$  ion, we can examine how they behave under the influence of the crystal field due to the neighbouring ligands. The crystal we are interested in,

In this thesis, is known as gadolinium ethylsulphate (from now on we will abbreviate this to GdES), and its structure was first obtained over fifty years ago. Since then it has been refined to a high degree of accuracy [Ketelaar 1937; Fitzwater and Rundle 1959; Gerkin and Reppert 1984]. The unit cell of GdES is found to contain two gadolinium ions, with each ion being coordinated by nine water molecules and three ethylsulphate radicals. Figure 1.3 illustrates the nearest neighbours of a typical  $Gd^{3+}$  ion in the lattice (though as we shall see later, the structure of the ethylsulphate radicals is far more complex than is shown in the diagram). The point group symmetry of the water molecules surrounding the  $Gd^{3+}$  ion is  $C_{2h}$ . We will examine the fine structure of the lattice in more detail in chapter seven, when we come to investigate the nature of the lattice vibrations in GdES. The coordinates of the oxygen atoms which belong to the neighbouring water molecules are given in table 1.1 (see next page).

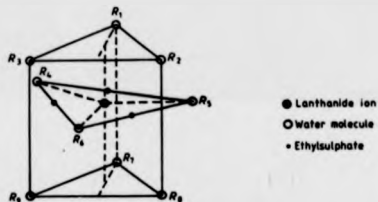


Figure 1.3. geometrical configuration of the nearest neighbours of a  $Gd^{3+}$  ion in the GdES crystal (from Christodoulos et al. (1986)). The diagram is not drawn to scale. The symbols  $R_1$  to  $R_9$  indicate the positions of the oxygen atoms within the water molecules.

In the crystal field theory of the rare-earth ethylsulphates, it is usual to ignore the influence of the ethylsulphate radicals (an approximation whose validity is difficult to assess, and which has not been investigated to any great depth). Therefore the problem consists of evaluating how the

Table 1.1: coordinates of oxygen atoms from the water molecules in fig. 1.3 (in units of  $a_0$ )

| water mol. | X coord | Y coord | Z coord |
|------------|---------|---------|---------|
| 1          | 2.8787  | 0       | 3.4307  |
| 2          | -1.4394 | 2.4930  | 3.4307  |
| 3          | -1.4394 | -2.4930 | 3.4307  |
| 4          | 1.5305  | 2.6508  | 0       |
| 5          | -3.0609 | 0       | 0       |
| 6          | 1.5305  | -2.6508 | 0       |
| 7          | 2.8787  | 0       | -3.4307 |
| 8          | -1.4394 | 2.4930  | -3.4307 |
| 9          | -1.4394 | -2.4930 | -3.4307 |

ground state levels of  $Gd^{3+}$  are split in an electric field of  $C_{2h}$  symmetry. In 1952, Stevens developed a technique which makes problems of this nature comparatively straightforward [Stevens 1952]. It is known as the technique of "operator equivalents", and it provides an easy way of calculating the matrix elements of the crystal field potential. Stevens first used the method to investigate cerium ethylsulphate, with some measure of success [Stevens 1952a]. The basic steps of the calculation of level splittings in a crystal field have been given in an article by Hutchings (1964).

To investigate the level splittings in  $Gd^{3+}$ , we must first of all write down the crystal field potential appropriate to  $C_{2h}$  symmetry. The easiest way to do this is to assume that the potential satisfies Laplace's equation (i.e. we are assuming that the ligand charges do not overlap the 4f-electrons), so that we may write [Low 1960 p12]

$$V_{cf} = \sum_{l,m} A_l r^l Y_l^m(\theta_1, \phi_1) \quad (1.6)$$

This potential energy must be invariant under  $C_{2h}$  symmetry. Also, because we are dealing with 4f-electrons, we may ignore all terms in  $V_{cf}$  for which

1>6 (Heine p150). This gives the following expression for  $V_{cr}$  in  $C_{4h}$  symmetry (Heine p150; Stevens 1952a1):

$$V_{cr} = B_0^c V_0^c + B_2^c V_2^c + B_4^c V_4^c + B_6^c V_6^c + B_8^c V_8^c \quad (1.7)$$

$$V_0^c = \sum_i (3s_i^2 - r_i^2) \quad (1.8a)$$

$$V_2^c = \sum_i (35s_i^2 - 30r_i^2 s_i^2 + 3r_i^4) \quad (1.8b)$$

$$V_4^c = \sum_i (231s_i^4 - 315r_i^2 s_i^2 + 104r_i^4 s_i^2 - 5r_i^6) \quad (1.8c)$$

$$V_6^c = \sum_i (s_i^6 - 15s_i^4 y_i^2 + 15s_i^2 y_i^4 - y_i^6) \quad (1.8d)$$

$V_0^c$  is a constant, and is of no interest to us from now on. The sums are over all 4f-electrons. For the moment let us forget about the effects of intermediate coupling, and assume that the ground state of  $Gd^{3+}$  is a pure LS-coupling state with  $L=0$ ,  $S=7/2$  and  $J=7/2$ . To calculate the crystal field splitting, we need to find the matrix of  $V_{cr}$  within this manifold of eight states. The splitting then emerges on diagonalising this matrix. In order to find the matrix elements of  $V_{cr}$ , we use the method of operator equivalents, which works as follows. Consider the term  $V_2^c$ . The first thing we must do is to replace the coordinates  $x_i, y_i, z_i$  and  $r_i$  with the angular momentum operators  $J_x, J_y, J_z$  and  $J$  respectively, being careful to remember that whilst the coordinates commute, the angular momentum operators do not (for instance, although the simple product  $xy$  is numerically equal to the product  $yx$ , the operator product  $J_x J_y$  is not equal to the product  $J_y J_x$ ). Therefore, if one has to deal with a product such as  $xy$ , one would replace it with  $\frac{1}{2}(J_x J_y + J_y J_x)$ . The method of operator equivalents then tells us that

$$\sum_i (3s_i^2 - r_i^2) \rightarrow \alpha \langle r^2 \rangle (3J_z^2 - J(J+1)) \quad (1.9)$$

The matrix elements of both sides of this equivalence are then identical within a manifold of states defined by a total angular momentum  $J$ . Here  $\alpha$  is a constant to be determined,  $\langle r^2 \rangle$  is the mean value of  $r^2$  for a 4f-electron, and  $J_z$  is the  $z$ -component of the total angular momentum  $J$ . The success of this transformation depends on the fact that both sides of the equivalence transform in the same way under rotations (in this case according to the irreducible representation  $D^{(2)}$ ). The constants  $\alpha$  have been

tabulated by Stevens (Stevens 1952), and for  $^8S_{7/2}$  it is equal to zero. This is because although (1.9) is defined in terms of the total angular momentum  $J$ , to find  $\alpha$  it is necessary to rewrite (1.9) as an operator equivalent defined in terms of  $L$ , and finally in terms of the individual angular momenta of the  $f$ -electrons (see Stevens (1952) for full details). However since  $L=0$  for an  $S$ -state ion, it automatically follows that  $\alpha=0$ . So all matrix elements of  $V_{\alpha}$  vanish within the LS-coupling ground state. One finds that all of the other terms in equations (1.8) have vanishing matrix elements within this ground state as well. Therefore the matrix of  $V_{\alpha}$  within the ground state is identically zero, and so since we have nothing to diagonalise, it follows that the predicted zero field splitting is zero.

This result is not verified by experiment. It is found that the eight-fold degeneracy is resolved into four doublets, with the  $M_J = \pm 7/2$  doublets lying above the  $M_J = \pm 1/2$  doublets such that, at 290K,

$$\Delta E = E(M_J = \pm 7/2) - E(M_J = \pm 1/2) = 0.236 \text{ cm}^{-1} \quad (1.10)$$

Compared with splittings in rare-earths with orbitally degenerate ground states, this value is very small ( $\sim 0.1 \text{ cm}^{-1}$  compared with  $\sim 100 \text{ cm}^{-1}$ ). So it is perhaps not surprising that a first order perturbation treatment does not work. We may interpret this result as follows. The LS-coupling ground state of  $\text{Gd}^{3+}$  is degenerate as a result of the total spin of its  $4f$ -electrons. But the crystal field is independent of spin, and so cannot raise any spin degeneracy that might be present, by itself (i.e. in first order perturbation theory).

As yet we have not considered the effects of intermediate coupling. To do this we require the matrix of  $V_{\alpha}$  within the manifold of states  $^8S_{7/2}$  given in equation (1.5) (Dieke 1966 p101). The matrix elements of  $V_{\alpha}$  then take the following form:

$$\begin{aligned} \langle ^8S_{7/2} | V_{\alpha} | ^8S_{7/2} \rangle &= 0.974 \langle ^8S_{7/2} | V_{\alpha} | ^8S_{7/2} \rangle \\ &+ 0.180 \langle ^8S_{7/2} | V_{\alpha} | ^6P_{7/2} \rangle \\ &+ 0.180 \langle ^6P_{7/2} | V_{\alpha} | ^8S_{7/2} \rangle \end{aligned} \quad (1.11)$$

$$+ 0.026 \langle 6p_{7/2} | V_{e2} | 4p_{7/2} \rangle$$

+ smaller admixtures.

We have already seen that the first term vanishes. The second and third terms vanish because the spin components are different [Wybourne 1966], and the fourth term is found (surprisingly) to vanish too. In fact it can be shown that all diagonal matrix elements of the form  $\langle 2S+1L_3 | V_{e2} | 2S+1L_3 \rangle$  are zero within states of the  $4f^7$  configuration [Newman 1970]. Any remaining terms which are non-zero are too small to account for the experimental splitting. We therefore conclude that to get agreement with experiment for S-state splittings, we must use higher order perturbation theory.

As a slight digression it is worth pointing out that had we been able to predict a zero-field splitting in first order, the next step would have been to fit the parameters  $B_2^0$ ,  $B_2^2$ ,  $B_4^0$  and  $B_4^2$  to the experimental data [Low 1960 p125]. The reason for doing this is that experience has shown that if  $V_{e2}$  is assumed to originate solely from an electrostatic crystal field, theoretical calculations do not agree well with experiment in rare-earth compounds [Newman 1971]. To get adequate agreement from theoretical calculations, one must incorporate many other contributory mechanisms. Therefore it has seemed easier simply to choose the parameters so that they automatically agree with experiment. A concept which is sometimes useful in the interpretation of crystal field data for S-state ions is that of the "spin Hamiltonian", in which a  $2S+1$  degenerate level is described by a fictitious spin  $S'$ . The effect of crystal fields, magnetic fields etc. is then described in terms of a polynomial in  $S'$  and its components ( $S'_x$ ,  $S'_y$ ,  $S'_z$ ) [Abragam and Bleaney 1970]. In general, a spin-Hamiltonian will contain a large number of terms, but symmetry considerations may be used to reduce it to a more manageable form. The parameters of the spin-Hamiltonian can then be obtained with the help of experimental data. The fact that spin-Hamiltonians make use of an effective spin variable can lead to some confusion, especially if the concept is being used for orbitally non-degenerate states, because it is often difficult to attach a physical meaning to these operators. For a more complete discussion of this point, see Stevens (1976).

### 1.5 Higher Order Perturbation Theory

Since we are unable to account for the zero-field splittings of S-state ions in first order perturbation theory, the next step is to see what happens if we use perturbation theory of higher order. These calculations were first performed about thirty five years ago, and in this section we will discuss some of the most important results to have emerged since then. Higher order perturbation theory involves the introduction of excited intermediate states, and in this section we will restrict ourselves to a discussion of those mechanisms for which the excited states reside on the gadolinium ion. In the literature these are often referred to as "on-site mechanisms". We will follow the usual convention and write out the mechanisms in schematic form. The mathematical details can be found either in the original references, or in the reviews by Wybourne (1966), Buckmaster et al. (1972), or Smith et al. (1977).

The largest contribution from higher order theory is from a relativistic calculation due to Wybourne (1966). He found that certain matrix elements of  $V_{ef}$  which vanish in the non-relativistic limit (for instance the matrix element connecting the  $^8S_{7/2}$  and  $^6P_{7/2}$  levels) do not vanish between relativistic eigenstates. He therefore proposed the following second order mechanism:

$$\langle ^8S_{7/2} | H_{ee} | ^6P_{7/2} \rangle \langle ^6P_{7/2} | V_{ef} | ^8S_{7/2} \rangle$$

In this expression  $V_{ef}$  is an effective operator (which is not entirely orbital) which is obtained from a standard technique for dealing with relativistic wavefunctions (Judd 1965). Very briefly, the technique involves finding an operator  $V_{ef}$  which satisfies

$$\langle \Psi_{ee} | V_{ef} | \Psi_{ee} \rangle = \langle \Psi | V_{ef} | \Psi \rangle,$$

where  $\Psi$  and  $\Psi'$  are non-relativistic wavefunctions, and  $\Psi_{ee}$  and  $\Psi'_{ee}$  are the corresponding relativistic wavefunctions. Wybourne's mechanism yields a contribution  $\Delta E_1 = -0.312 \text{ cm}^{-1}$  to the splitting. It is thus of the right order of magnitude, but it has the wrong sign.

The next largest mechanism is due to Hutchison, Judd and Pope (1957). They observed that  $\langle {}^6D_{7/2} | V_{eff} | {}^8P_{7/2} \rangle$  is a non-vanishing matrix element in the  $4f^7$  configuration, owing to the presence of the  $V_4^0$  term. They proposed the following fourth order mechanism:

$$\langle {}^8B_{7/2} | H_{so} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | H_{so} | {}^6D_{7/2} \rangle \langle {}^6D_{7/2} | V_{eff} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | H_{so} | {}^8B_{7/2} \rangle$$

This mechanism has been evaluated by Buckmaster et al (1972), and it gives a contribution of  $\Delta E_3 = -0.228 \text{ cm}^{-1}$ . It is again of the wrong sign.

These two mechanisms are the largest contributions obtained using intermediate states on the  $Gd^{3+}$  ion. However there are two others which are worthy of mention. The first is the electrostatically correlated crystal field (ECCF) of Rajnak and Wybourne (1964). Using this idea, they proposed the following mechanism:

$$\langle {}^8B_{7/2} | H_{so} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | V_{soeff} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | H_{so} | {}^8B_{7/2} \rangle$$

$$\text{where } V_{soeff} = -2/\Delta E \sum_X \langle n | H_{so} | V_{eff} | X \rangle \langle X | H_{so} | n \rangle, \psi$$

Here  $|X\rangle$  is a state belonging to an excited configuration which perturbs the  $4f^7$  configuration, and  $\Delta E$  is the energy difference between the excited and  $4f^7$  configurations. Wybourne (1966) has considered the excited configurations  $4f^6d$  and  $4f^6s$ , and has found that they give a contribution of  $\Delta E_3 = +0.05 \text{ cm}^{-1}$ . The contribution from the ECCF is thus of the right sign, but is too small to cancel the contributions from  $\Delta E_1$  and  $\Delta E_2$ . The concept of the ECCF is found to be of greater importance in the theory of, for instance,  $Mn^{2+}$  (Slu 1987), which has a half filled 3d-shell.

The second mechanism is due to Judd [Hutchison et al. 1957]. He observed that the  ${}^6P_{7/2}$  levels are split by a crystal field interaction with higher levels. Since  ${}^6P_{7/2}$  is coupled to  ${}^8B_{7/2}$  by means of the spin-orbit interaction, this must help to split the  ${}^8B_{7/2}$  levels. He proposed the following mechanism:

$$\sum_j \langle {}^8B_{7/2} | H_{so} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | V_{eff} | {}^6L_j \rangle \langle {}^6L_j | V_{eff} | {}^6P_{7/2} \rangle \langle {}^6P_{7/2} | H_{so} | {}^8B_{7/2} \rangle$$



Buckmaster et al. (1972) have found that this mechanism leads to a zero field splitting of  $\Delta E_4 = +0.023 \text{ cm}^{-1}$ . Again this is of the right sign, but is too small to cancel the large negative contributions.

The other mechanisms which have been considered in the past give contributions which are very small. They include a second order spin/spin interaction [Pryce 1950], a third order spin/spin interaction [Wybourne 1966], and an anisotropic spin-orbit interaction [Lulek, 1969]. Between them, they lead to a contribution of  $\Delta E_5 = -0.008 \text{ cm}^{-1}$ . Therefore, the grand total which is obtained by adding together all of these mechanisms is  $\Delta E = \sum \Delta E_i = -0.473 \text{ cm}^{-1}$ . Smith et al. (1977) have re-evaluated all of these mechanisms using relativistic eigenfunctions, and when this is done the total becomes

$$\Delta E_{\text{tot}} = -0.432 \text{ cm}^{-1} \quad (1.12)$$

We therefore conclude that higher order perturbation theory, using on-site mechanisms alone, is not sufficient to explain the zero-field splitting of  $\text{Gd}^{3+}$  in an ethylsulphate host lattice.

## 1.6 Summary and Discussion

In this chapter we have presented an introduction to some of the difficulties involved in accounting for the zero-field splitting of the ground level of  $\text{Gd}^{3+}$  in an ethylsulphate host lattice. To begin with, we examined the ground level of  $\text{Gd}^{3+}$  and showed that it has an eight-fold degeneracy. We also argued qualitatively that the magnitude of the spin-orbit interaction in the rare-earths means that term mixing is likely to occur, and so the true ground state is not a pure LS-coupling ground state. In the LS-coupling approximation, the ground level is an orbital singlet ( $L=0$ ), and so the degeneracy arises as a result of the electron spins. The first order perturbation theory was then shown to fail, and this was explained in terms of the spin independence of  $V_{\text{cf}}$ . In the final section we considered some of the higher order perturbation calculations that have been carried out, and we concluded that the use of "on-site" mechanisms alone cannot explain the observed splittings. Therefore we need to consider a

more sophisticated approach to the crystal field problem. This will be the subject of the next chapter. In this chapter we will introduce a concept which has proved invaluable in the study of  $Gd^{3+}$ , namely the spin correlated crystal field.

## CHAPTER 2

### The Method of Stevens

#### 2.1 Introduction

In the previous chapter we attempted to find the zero field splitting of the  $Gd^{3+}$  ion in an ethylsulphate host lattice, using first order perturbation theory and a variety of higher order perturbation schemes involving on-site mechanisms. We found that by themselves these methods fail to produce adequate agreement with experiment, and so we must broaden our search for a mechanism which leads to agreement with experiment. One of the main problems of the higher order mechanisms is the vanishing of the diagonal matrix elements of the crystal field within the  $4f^7$  configuration [Newman 1970]. This vastly restricts the range of mechanisms to choose from. It was this problem which led Newman (1970) to propose a new crystal field operator which does have matrix elements within the  $4f^7$  configuration. He called it the Spin Correlated Crystal Field (SCCF), and it has proved enormously useful in the determination of zero field splittings for  $Gd^{3+}$ . We will discuss the SCCF later on in the chapter, but first we must describe a technique which facilitates the calculation of the magnitude of the SCCF. The technique was developed by Stevens (1975), and it provides a systematic way of examining the low-lying energy levels of a magnetic insulator. From now on we will refer to it as the 'Method of Stevens'.

#### 2.2 Motivation

Stevens' motivation in developing the new theory was to try and address some of the criticisms which had been levelled at the existing theories for dealing with localised moments in magnetic insulators. To see what these criticisms are in the context of crystal field theory, let us consider the Hamiltonian for the electrons in a solid:

$$H = \sum_i \langle p^2/2m \rangle_i - \sum_i Z_n e^2/r_{ni} + \frac{1}{2} \sum_{i,j} e^2/r_{ij} \quad (2.1)$$

The first term represents the kinetic energy of the electrons, the second term is the energy of the electrons in the field of the nuclei, and the third term is the electron/electron repulsion. We will ignore smaller possible additional terms (e.g. Zeeman interaction) for the moment. The Hamiltonian (2.1) incorporates all of the symmetries of the solid; in particular it does not distinguish electrons, and it incorporates all of the space group symmetries of the lattice. But it has the disadvantage that its eigenfunctions and eigenvalues cannot be found exactly. Hence the energy levels of the solid can only be found with the help of approximations.

Now let us suppose that (2.1) has been defined for a crystal consisting of rare-earth ions embedded in an insulating host lattice. In the Crystal Field Approximation, the 4f-electrons of the rare-earth ions are regarded as being localised about their respective sites. Their energy levels in the solid are then regarded as being different from those of the free ion as a result of the electrostatic interaction with the neighbouring ions. The Hamiltonian for the 4f-electrons can then be written in the form

$$H_{4f} = \sum_i h_A(i) + \sum_i h_B(i) + \dots \quad (2.2)$$

where A, B, ... label the rare-earth ions in the crystal, and  $i$  is a label for the 4f-electrons on a given rare-earth ion. The energy levels of the 4f-electrons are then found by using perturbation theory on the free ion levels, with (2.2) as the perturbation.

The Crystal Field approach works well in practice, but is unsatisfactory for several reasons. The main problem is that in reaching (2.2), a given set of electrons has been associated with the rare-earth ion at A, another set has been associated with the rare-earth ion at B, and similarly for all of the other rare-earth ions in the crystal. These electrons have therefore been distinguished, thereby contradicting the Pauli principle, which tells us that electrons are indistinguishable. Other problems arise if we ask about the spatial symmetry properties of (2.2), because the coordinates of an electron are measured from the nucleus to which it has been allocated, rather than from some common origin.

The Method of Stevens aims to overcome these shortcomings by dealing with the properties of an insulating crystal lattice in a very fundamental way, namely as a full many-electron problem in which all electrons are indistinguishable, and all of the symmetries of (2.1) are preserved. To do this an unperturbed Hamiltonian is defined, and by a judicious use of second quantization techniques and a series of angular momentum equivalences, Stevens is able to show that the physical properties of magnetic insulators emerge from the various orders of perturbation theory. In the following sections we will examine each aspect of the method. A full account can be found in his review article of 1976 [Stevens 1976].

### 2.3 The Unperturbed Hamiltonian

The first objective of any perturbation theory is to decide on a suitable unperturbed Hamiltonian  $H_0$ . By 'suitable' we mean that it should have the following properties:

- 1)  $H_0$  should have the same symmetry properties as  $H$ .
- 2) The perturbation  $H-H_0$  should be small, in the sense that the perturbation expansion should converge in relatively low order.
- 3) The perturbation scheme should be tractable.

It also goes without saying that  $H_0$  itself should have properties which are sufficiently simple for progress to be possible. Unfortunately, it is not easy to find an  $H_0$  which satisfies all of these requirements. For instance, a good starting point would seem to be one based on the Crystal Field concept of assuming that certain electrons are localised on certain ions in the lattice. One could then envisage having an  $H_0$  similar in form to (2.2), with the interactions between ions emerging from the perturbation  $H-H_0$ . Because this definition of  $H_0$  already incorporates the idea of a localised moment, and it is this which interests us, one would expect the perturbation  $H-H_0$  to be small, thereby satisfying the second criterion above. The problem with this definition is that the first criterion is not satisfied, because as we mentioned in the previous section, if we associate certain electrons with certain ions, we cause the electrons to be distinguished. Therefore we would have the unusual situation of having a

perturbation which actually raises the symmetry of the system. One would probably have to proceed to very high order perturbation theory (possibly even infinite order) to incorporate this raising of symmetry. Clearly this is a most unsatisfactory situation.

Having rejected other possible schemes on the grounds that one or more of the above criteria are not satisfied (for details see [Stevens 1976 p1]), Stevens decided that the only course of action would be to define an unperturbed Hamiltonian. He reasoned that such an  $H_0$  should have eigenstates and eigenvalues which approximate to those of  $H$ . If this is the case, then one might reasonably assume that the perturbation  $H-H_0$  will be small. He decided that the best way to do this would be to construct approximate many-electron states for the crystal, and then insist that these be the eigenstates of  $H_0$ . The construction of such states is relatively straightforward, because the state of any ion in the crystal may be written as a linear combination of Slater determinants [Stevens 1976 p12], provided of course that one has a suitable set of one-electron basis functions. The many-electron state of the whole crystal is then obtained by writing down the appropriate linear combination for each ion in the crystal, multiplying them together, and then antisymmetrizing. The result is a many-electron state  $|n\rangle$ , equal to a linear combination of Slater determinants of the form

$$\{ \phi_{A1}(1), \phi_{A2}(2), \dots, \phi_{B1}(1), \phi_{B2}(2), \dots \}$$

where the  $\phi_A, \phi_B, \dots$  represent one-electron functions centred on ions at sites A, B, ... Any many-electron state of the crystal may be constructed in this way. If the one-electron states are mutually orthogonal, then the states  $|n\rangle$  will be mutually orthogonal. Unfortunately, atomic like functions are not suitable for this purpose, because they are not in general orthogonal between sites. Stevens therefore decided to use Wannier functions, which are orthogonal both on and between sites. We will discuss the properties of these functions in detail in appendix D, but for now it is sufficient to know that the low-lying Wannier functions on a given site can be put into a one to one correspondence with the atomic  $1s, 2s, 2p, \dots$  functions, so that  $n, l, m, m_z$  labelling may be used.

It is now straightforward to define an  $H_0$  which has the  $|n\rangle$  as its eigenstates. We simply define a set of projection operators  $P_n$  for the states  $|n\rangle$  according to  $P_n = |n\rangle\langle n|$ , and then define

$$H_0 = \sum_n \lambda_n P_n \quad (2.3)$$

This  $H_0$  then has the following property:

$$H_0 |m\rangle = \lambda_m |m\rangle \quad (2.4)$$

because  $P_n |m\rangle = |n\rangle\delta_{nm}$ . The eigenvalues  $\lambda_n$  may be chosen at will. Stevens decided to choose  $\lambda_n = \langle m|H|m\rangle$ , because then the eigenvalues of  $H_0$  should approximate to those of  $H$ . Hence the perturbation  $H-H_0$  should be small. In addition, the intrinsic simplicity of equations (2.3), (2.4) and the projection operators  $P_n$  should result in a tractable perturbation theory.

Although (2.3) satisfies two of the three criteria required of the definition of  $H_0$ , it has some serious flaws. It may be shown [Stevens p14] that whilst (2.3) exhibits the correct indistinguishability and translational invariance requirements, it is not necessarily invariant under all rotations which leave the lattice invariant. This is due to the fact that the spins of the electrons are defined with respect to a fixed axis of quantisation, which may not be left unchanged by a rotation of the lattice. A further problem can be anticipated from the perturbation theory itself. It may happen that some of the states  $|n\rangle$  will be nearly degenerate, so that  $\langle n|H|n\rangle = \langle m|H|m\rangle$ , where  $|n\rangle$  and  $|m\rangle$  are different. The higher orders of perturbation theory will probably introduce terms with denominators of the form  $\langle n|H|n\rangle - \langle m|H|m\rangle$ , and if this is nearly zero, unphysical divergences will be introduced.

Fortunately these problems can be overcome by means of a change in the definition of  $H_0$ . The new definition hinges on the fact that the states  $|n\rangle$  may be separated into distinct "families" of states [Stevens 1976b]. The simplest separation would be one in which each state of a given family was consistent with a given occupation number for each shell of each ion in the crystal. More complex separations are possible (see later). The

states belonging to a given family will not in general be degenerate. This led Stevens to redefine the unperturbed Hamiltonian  $H_0$  as follows:

$$H_0 = \sum_r E_r P_r \quad (2.5)$$

$$\text{where } E_r = \frac{\sum_{n_r} \langle n_r | H | n_r \rangle}{\sum_{n_r} \langle n_r | n_r \rangle} \quad (2.6)$$

$$\text{and } P_r = \sum_{n_r} |n_r\rangle \langle n_r| \quad (2.7)$$

In these expressions  $|n_r\rangle$  denotes a state belonging to the  $r$ th family.  $E_r$  is therefore the mean energy of the  $r$ th family, and  $P_r$  is the projection operator for the  $r$ th family. It has the following properties:

$$P_r P_s = P_r \delta_{rs} \quad (2.8)$$

$$P_r |n_s\rangle = |n_s\rangle \delta_{rs} \quad (2.9)$$

The point about this definition is that the eigenstates of  $H_0$  (the  $|n_r\rangle$ ) now fall into well spaced, degenerate levels, with eigenvalues equal to the mean energies of the various families. The problem of divergences in higher order perturbation theory is thus removed. The new unperturbed Hamiltonian has two more very convenient properties. Firstly, it is found that it contains all of the symmetries of  $H$ , including the correct rotational symmetries (Stevens p371). Secondly, there is a powerful perturbation theory which can be used on systems with well spaced, degenerate levels. Therefore the definition of  $H_0$  given by (2.5) must be considered superior to that given by (2.3).

#### 2.4 Perturbation Theory

Before beginning the perturbation theory, it is important to know what it is that we wish to obtain from it. Stevens was particularly interested in the low-lying levels of crystals containing localised moments, and so the objective of the perturbation theory in the Method of Stevens is to obtain an effective operator, acting within the ground family of states (defined by  $P_0$ ), whose matrix, in a certain angular momentum representation, is



identical with that of  $H$ . The diagonalization of the effective operator, within the ground family, will then, hopefully, be easier than that of  $H$ .

From the definition of  $H_0$ , we see that  $H_0$  only has matrix elements between two states belonging to the same family, i.e.

$$\langle n_0 | H_0 | n_0 \rangle = E_0 \delta_{n_0 n_0}$$

In particular,  $H_0$  does not connect states between the ground family and an excited family. On the other hand, the perturbation  $H-H_0$  will have off diagonal matrix elements of this form. Since we require an effective operator which describes the ground family of states, we would like the perturbation theory to reduce the effect of the off diagonal matrix elements of  $H-H_0$ . The effect of any interaction between the ground and excited families should be incorporated into the effective operator via the perturbation theory.

The actual perturbation theory proceeds as follows (Bates et.al. 1968; Stevens 1974). Let us write the full Hamiltonian as  $H = H_0 + eV$ , and let us perform a unitary transformation on it, so that it becomes

$$\exp(i\epsilon X) [H_0 + eV] \exp(-i\epsilon X). \quad (2.10)$$

The operator  $X$  can now be chosen so that all terms which couple states in the ground family to states in excited families are reduced to at least  $O(\epsilon^2)$ . The condition for this to hold is

$$P_0 \exp(i\epsilon X) [H_0 + eV] \exp(-i\epsilon X) P_r = O(\epsilon^2) \quad (2.11)$$

In (2.11), it is to be understood that  $r \neq 0$ . After some algebra (expanding exponentials and setting terms linear in  $\epsilon$  to zero), the effective operator is found to be

$$\begin{aligned} H_{\text{eff}} &= P_0 \exp(i\epsilon X) (H_0 + eV) \exp(-i\epsilon X) P_0 \\ &= E_0 P_0 + e P_0 V P_0 - e^2 \sum_{n \neq 0} P_0 V P_n V P_0 / (E_0 - E_n) \end{aligned} \quad (2.12)$$

This is the operator we seek, correct to second order. It acts purely within the ground family, with interactions between the ground and excited families being incorporated into the third term of (2.12). We can make a slight simplification to (2.12), because from (2.5) and (2.8) it follows that  $P_0 H_0 P_0 = E_0 P_0 P_0 = E_0 P_0 \delta_{aa}$ . Putting  $\epsilon V = H - H_0$  into (2.12) then gives

$$H_{eff} = P_0 H P_0 - \sum_{a \neq 0} P_0 H P_a H P_0 / (E_0 - E_a) \quad (2.13)$$

For most of the thesis, our interest will be with the second term on the right hand side of (2.13). The great advantage of (2.13) is that the perturbation  $H - H_0$  does not appear explicitly in it; instead one is left to deal with the full Hamiltonian  $H$ . It might also be thought that the details of the unperturbed Hamiltonian  $H_0$  have been lost as well, but this is not the case, because the energy denominator of the second term in (2.13) is equal to a difference of unperturbed energies. These energy denominators will appear in the higher order corrections too.

### 2.5 Angular Momentum Equivalences: First Order Theory

In order to investigate further the properties of the effective operator (2.13) it is convenient to rewrite  $H$  in terms of second quantized operators. This simply involves rewriting the one and two-body operators which make up  $H$  in the following way (Raimis 1972; Harrison 1980):

$$\sum_i h_i = \sum_{ab} \langle \phi_a | h | \phi_b \rangle \alpha_a^\dagger \alpha_b \quad (2.14a)$$

$$\frac{1}{2} \sum_{ijkl} g_{ijkl} = \frac{1}{2} \sum_{abcd} \langle \phi_a, \phi_b | g | \phi_c, \phi_d \rangle \alpha_a^\dagger \alpha_b^\dagger \alpha_d \alpha_c \quad (2.14b)$$

In these expressions the states  $|\phi\rangle$  are the one-electron Wannier functions used to construct the many-electron states  $|n\rangle$ . They are convenient for second quantisation purposes because they form a complete orthonormal set (see appendix D). The operators  $\alpha^\dagger$  and  $\alpha$  satisfy the following anticommutation rules:

$$[\alpha_a^\dagger, \alpha_b^\dagger] = [\alpha_a, \alpha_b] = 0, \quad [\alpha_a^\dagger, \alpha_b] = \delta_{ab} \quad (2.15)$$

The effective operator (2.13) will now consist of strings of second quantized operators sandwiched between two  $P_n$ 's. Each string will contain the same number of annihilators and creators. This fact now allows a further modification to be made. Suppose a string contains a pair of operators of the form  $a^{\dagger}a$ , where both  $a^{\dagger}$  and  $a$  refer to electrons in the same open shell. In view of what we said earlier about the low-lying Wannier functions on an ion being atomic-like, it follows that we may label the  $a^{\dagger}$  and  $a$  with the values of  $m_l$  and  $m_s$  ( $n$  and  $l$  are fixed for a given shell). The most general form of  $a^{\dagger}a$  is then  $a_{m_s m_l}^{\dagger} a_{m'_s m'_l}$ , where  $m$  and  $m'$  are the values of  $m_l$ , and  $\sigma$  and  $\sigma'$  are the values of  $m_s$ . The effect of  $a_{m_s m_l}^{\dagger} a_{m'_s m'_l}$  is to annihilate an electron with  $m_l = m'$ ,  $m_s = \sigma'$ , and to create another one with  $m_l = m$ ,  $m_s = \sigma$ . Stevens appreciated that such a process is also accomplished by the angular momentum operators  $L_x, L_y, L_z$  and  $S_x, S_y, S_z$ , and so there must be a relationship between the operators  $a^{\dagger}a$  and these angular momentum operators. This is in fact found to be the case, and Stevens obtained the following relationships (Stevens 1974a):

$$a_{m_s m_l}^{\dagger} a_{m'_s m'_l} = \frac{1}{2} \sum_{n1} \Delta_{m m'}^{n1} O_{m_s m'_s}^{(n)} \left( \frac{1}{2} \right) (1 + 2s_l^z) \quad (2.16a)$$

$$a_{m_s m_l}^{\dagger} a_{m'_s m'_l} = \frac{1}{2} \sum_{n1} \Delta_{m m'}^{n1} O_{m_s m'_s}^{(n)} \left( \frac{1}{2} \right) (1 - 2s_l^z) \quad (2.16b)$$

$$a_{m_s m_l}^{\dagger} a_{m'_s m'_l} = \sum_{n1} \Delta_{m m'}^{n1} O_{m_s m'_s}^{(n)} \left( \frac{1}{2} \right) s_l^x \quad (2.16c)$$

$$a_{m_s m_l}^{\dagger} a_{m'_s m'_l} = \sum_{n1} \Delta_{m m'}^{n1} O_{m_s m'_s}^{(n)} \left( \frac{1}{2} \right) s_l^y \quad (2.16d)$$

The symbols  $+$  and  $-$  represent  $m_s = +\frac{1}{2}$  and  $m_s = -\frac{1}{2}$  respectively. The subscript  $l$  labels the 4f-electrons, and the operators  $O$  are those of Smith and Thornley (1966). The  $\Delta_{m m'}^{n1}$  are given by

$$\Delta_{m m'}^{n1} = \langle m | O_{m_s m'_s}^{(n)} | m' \rangle / N_{m_s}^2 \quad (2.17)$$

The  $N_{m_s}^2$  are also given by Stevens (1974a). There is a more sophisticated way of looking at these equivalences. The operators  $a_{m_s m_l}^{\dagger}$  and  $a_{m_s m_l}$  (multiplied by a phase factor) can be considered as double tensor operators (Judd 1967). That is, they are defined by two ranks, one in orbital space and one in spin space. The orbital rank  $l$  depends on the shell for which the  $a$ 's are defined, and the spin rank is  $s=\frac{1}{2}$ . The product of two such

operators may then be expanded in terms of double tensor operators whose orbital and spin ranks are consistent with the coupling of the orbital and spin ranks of the  $a'$  and  $a$ . The relations (2.16) are an example of such an expansion.

We are now in a position to see how the Method of Stevens works in practice. As an example let us consider a crystal containing  $Gd^{3+}$  ions (e.g.  $GdES$ ). The ground family of states, projected out by  $P_0$ , can be taken to be those states in which each  $Gd^{3+}$  ion is in one of the  $|^8S_{7/2}\rangle$  intermediate coupling ground states. Excited families are defined by those sets of many-electron states in which one or more  $Gd^{3+}$  ions are in intermediate coupling states which do not originate from the  $^8S$  term, or by states in which one or more electrons have been excited out of the  $4f$ -shell. Now suppose that we want an effective operator to describe the splitting of the  $|^8S_{7/2}\rangle$  states of a  $Gd^{3+}$  ion at a site  $A$ . We therefore require combinations of operators which create and annihilate electrons in  $4f$ -orbitals at  $A$ . Let these be denoted by  $a'$  and  $a$  respectively. The only terms of interest which can appear in first order (i.e. from  $P_0 H P_0$ ) are of the form  $a'a$ . These may arise from the one-body parts of  $H$ , or from two-body terms of the form  $a'f'fa$ , where  $f'$  and  $f$  refer to electrons in filled core shells at  $A$ , or  $a'c'ca$ , where  $c'$  and  $c$  refer to electrons in filled shells on neighbouring ions. The one-body terms, and the two-body terms which refer to a direct interaction between electrons, will lead to combinations of the form

$$\sum_{m,m'} \lambda(m,m') \sum_i a'_i a_i \quad (2.18)$$

because for a completely filled shell,  $f'f = c'c = 1$ . When the equivalences (2.16) are used, the result is the following effective operator:

$$\sum_{m,m'} \lambda(m,m') \Delta_{mm'} \sum_i a'_i a_i \quad (2.19)$$

where  $\lambda$  is a constant depending on the matrix elements accompanying the second quantized operators. Equation (2.19) is a crystal field like operator, whose form will reflect the local symmetry of the ion at  $A$  when all terms are collected together. But as we know from chapter one, such an

operator cannot resolve the degeneracy of the  $1^1S_{7/2}$  states of the ion at A, and so a higher order perturbation treatment is required, involving the generation of operators which can raise the degeneracy of these states.

## 2.6 Second Order Corrections to $H_{eff}$

For the rest of the thesis, our attention will be centred on the second order correction to the effective operator, i.e.

$$= \sum_{a \neq 0} P_a H P_a H P_a / (E_a - E_0) \quad (2.20)$$

for it is via this term (and of course higher order terms) that the coupling between states in the ground and excited families is incorporated. To see how we obtain an effective operator for the ground family from this term, let us return to our example of a crystal containing  $Gd^{3+}$  ions. In order to get an effective operator for the  $Gd^{3+}$  ion at site A, we require (2.20) to yield strings of operators of the form  $a^\dagger a$ ,  $a^\dagger a^\dagger a a$  etc. For simplicity we will consider the case where both of the H's in (2.20) are contributing one-body operators, but the arguments to be presented apply whatever the H's are contributing.

Let us suppose that the first H (reading from the right) in (2.20) contributes a term  $b_{\alpha}^{\dagger} a_{\alpha 0}$ , where  $b_{\alpha}^{\dagger}$  creates an electron in an orbital  $\alpha$  on a neighbouring ion. If  $b_{\alpha}^{\dagger} a_{\alpha 0}$  acts on a state  $|n_0\rangle$  in the ground family, the result is a new many-electron state  $|n_1\rangle$ , in which a 4f-electron has been transferred from the  $Gd^{3+}$  ion into an excited orbital  $\alpha$  on a neighbouring ion. The new state will belong to some excited family, say the  $r$ th. The second H in (2.20) must now operate so as to return the system back down to the ground family, for otherwise the operation with the leftmost  $P_a$  in (2.20) will give zero. That is, it must return the electron from the orbital  $\alpha$  back to the 4f-shell, and so the required one-body operator is  $a_{\alpha}^{\dagger} a_{\alpha 0}$ . The effective operator (2.20) then becomes

$$P_0 a_{\alpha}^{\dagger} a_{\alpha 0} P_r b_{\alpha}^{\dagger} b_{\alpha 0} P_0 \quad (2.21)$$

Because  $b_{\alpha\alpha}^{\dagger}$  connects  $P_{\alpha}$  to the  $r$ th excited family of states, we can define  $P_r = b_{\alpha\alpha}^{\dagger} P_{\alpha}$ , and because  $P_r P_{\alpha} = P_r \delta_{r\alpha}$ , the effective operator (2.21) reduces to the following form:

$$P_{\alpha} b_{\alpha\alpha}^{\dagger} b_{\alpha\alpha} b_{\alpha\alpha}^{\dagger} P_{\alpha} \delta_{r\alpha} \quad (2.22)$$

The effective operator (2.22) is accompanied by the numerical factor

$$\langle m' | h | \alpha \rangle \langle \alpha | h | m \rangle / \Delta(r, 0) \quad (2.23)$$

where  $\Delta(r, 0)$  is the energy separation of the  $r$ th and ground families. We can now make an important simplification to (2.22), if we bear in mind that the excited orbital  $\alpha$  is empty in the ground family  $P_{\alpha}$ . If this is the case, then  $b_{\alpha} b_{\alpha}^{\dagger} = 1 - b_{\alpha}^{\dagger} b_{\alpha} = 1$ , and the effective operator (2.22) simply becomes  $P_{\alpha} b_{\alpha\alpha}^{\dagger} P_{\alpha}$ . But as we saw in the previous section, this combination leads to a crystal field like operator when we sum over the spin  $\sigma$  and use the angular momentum equivalences' (2.16). The effect of including these second order contributions then is to renormalize the coefficient  $\lambda$  given in (2.10). Note that these contributions from second order cannot be interpreted as being due to a crystal field, even though they lead to crystal field like operators. For a numerical example, see Dixon et al. (1982).

The same sort of arguments apply for whatever sort of effective operator we are interested in. They also show that we should exercise caution in our interpretation of certain experimental data. For instance, as we mentioned in chapter one, it is usual to choose the parameters of the crystal field potential  $V_{cf}$  so as to obtain agreement with experimentally observed splittings. It follows from the above arguments that these parameters cannot be attributed to a crystal field unless one can be quite sure that the corrections from second (or higher) order are negligible.

## 2.7 The Spin Correlated Crystal Field

The last two sections show the true power of the Method of Stevens, for we could, in principle, use it to write down an effective operator which

incorporates all of the magnetic phenomena associated with a paramagnetic ion in an insulating crystal. Since the method is careful to incorporate the indistinguishability of the electrons, it is more fundamental than the theories described in chapter one. But in the case of  $Gd^{3+}$ , we still have a problem. The crystal field operators which emerge from the theory are essentially the same as those of chapter one, and we know that, by themselves, they cannot account for the zero field splitting of  $Gd^{3+}$ . It would therefore seem that we have made no progress.

The problem stems from the fact that many of the important matrix elements of  $V_{cf}$  and  $H_{ex}$  vanish between states of the  $4f^7$  configuration, in particular diagonal matrix elements such as  $\langle 4F_{7/2} | V_{cf} | 4F_{7/2} \rangle$  (Newman 1970). It was in an attempt to generate a scheme in which these diagonal elements do exist that Newman proposed a spin dependent crystal field of the form

$$V_{cf} = \sum_i g_i \sum_{\alpha} A_{\alpha} Y_{\alpha}^{\alpha}(\theta_i, \phi_i) \quad (2.25)$$

where  $\mathbf{g} = \sum_i \mathbf{g}_i$  and  $i$  labels the  $4f$ -electrons. This idea was taken up by Judd (1977), who was trying to examine the physical origin of the two-electron interactions in the crystal which could induce some sort of zero field splitting. He concluded that important terms of this sort must arise as a result of the strong exchange interaction between the parallel  $4f$ -electrons in the lanthanide ions. He incorporated these interactions by substituting

$$(C_q^k)_i \rightarrow C_k(\mathbf{g}_i, \mathbf{g}_i)(C_q^k)_i \quad (2.26)$$

in the crystal field potential. (The  $C_q^k$  are tensor operators proportional to the  $V_q^k$  of chapter one). Again  $\mathbf{g} = \sum_i \mathbf{g}_i$ . Note that (2.26) is a two-body operator, because  $\mathbf{g}_i \cdot \mathbf{g}_j = \sum_i \mathbf{g}_i \cdot \mathbf{g}_j$ . Operators of the form (2.26) are known as Spin Correlated Crystal Field (BCCF) operators. These operators do in general have matrix elements between states of the  $4f^7$  configuration [Dixon and Chatterjee 1980], and so it is reasonable to think that they will be of some importance in the crystal field theory of  $Gd^{3+}$ . In fact, Judd (1977) has shown that they are important for all lanthanides.

In order to calculate how important these operators are, we need to find the magnitude of the operators (2.26) for our system. Stevens' method provides us with a straightforward way of doing this, for all we need to do is to find the appropriate combinations of second quantized operators which, when the angular momentum equivalences (2.16) are used, lead to effective operators of the form (2.26). The magnitude of the effective operator can then be found by evaluating the matrix elements which appear with the second quantized operators, and the extra terms which appear on making the angular momentum transformation. The actual size of the splitting then appears on calculating the matrix elements of the BCCF between the states of the ground family, using the results of Dixon and Chatterjee (1980).

Such an analysis has been performed by Tuszynski et.al. (1984,1986) for  $Gd^{3+}$  in an ethylsulphate host, using the second order correction to  $H_{eff}$ . They considered a variety of excited families  $P_n$ , including those defined by excited states of the  $4f^7$  configuration, and also those defined by excited configurations of the  $Gd^{3+}$  ion, including (1)  $4f^6np^1$ ,  $n=2,3,4,5$ ; (2)  $4f^6np$ ,  $n=6,7$  and (3)  $4f^6nf$ ,  $n=5,6,7$ . They used a slightly more specialized form of the BCCF, namely

$$V_{eff} = \mu \sum_{i,j} C_0^i(l_i) g_{i,j} \quad (2.27)$$

We will not describe their analysis here, for it is very similar to that which will be given in the next chapter. Their calculations yielded a value of  $\mu=148.3 \text{ cm}^{-1}$ , and they found that this led to a ZFS of

$$\Delta E_{eff}^{on} = + 0.853 \text{ cm}^{-1}$$

Here the superscript 'on' represents the fact that the mechanisms used by Tuszynski et.al. all reside on the  $Gd^{3+}$  itself. When we include the mechanisms discussed in chapter one, the new grand total is

$$\Delta E = \Delta E_{ex} + \Delta E_{eff}^{on} = + 0.421 \text{ cm}^{-1} \quad (2.28)$$



We now have a theoretical splitting which is of the correct sign, but about a factor of two times too large.

## 2.8 Summary and Discussion

In this chapter we have introduced two concepts which are of the greatest importance in understanding crystal field phenomena in  $Gd^{3+}$ . Firstly we introduced the Method of Stevens, which enables a systematic treatment of magnetic phenomena in insulating crystals to be carried out. Secondly we introduced the SCCF, which is important by virtue of having non-vanishing diagonal matrix elements between the LS-states of the  $4f^7$  configuration. Stevens' method provides us with a means of calculating the magnitude of the SCCF, and we briefly described the work of Tuszynski et.al., who used the method to show that the use of excited states on the  $Gd^{3+}$  itself does indeed lead to an important contribution to the ZFS. However, the grand total is still too large, although it is now of the correct sign.

## CHAPTER 3

### The Introduction of Inter-Site Mechanisms

#### 3.1 Introduction

Up to now, we have considered a variety of perturbation mechanisms in an attempt to account for the zero field splitting of  $Gd^{3+}$  ions in an ethylsulphate host. These mechanisms all have one important factor in common, namely that the excited states involved reside on the  $Gd^{3+}$  ion itself. However, there is a lot of experimental evidence to suggest that the zero field splitting of  $Gd^{3+}$  can be very different in hosts which have the same point group symmetry and structure as GdES (Newman and Urban 1972). It therefore seems reasonable to assume that, to get good agreement with experiment, we must also consider mechanisms which directly involve the host lattice itself. The simplest such mechanism would involve the excitation of an electron from the  $Gd^{3+}$  ion onto a neighbouring ligand, and then back down to the  $Gd^{3+}$  ion again. Mechanisms of this type are referred to as inter-site mechanisms, and are necessarily described using the second (or higher) order corrections to  $H_{eff}$ .

The objective of this chapter is to describe the work of Christodoulos et al. (1986), who used the Method of Stevens to investigate a particular inter-site mechanism in which a 4f-electron is excited from the  $Gd^{3+}$  ion into an empty 3s-orbital on an oxygen atom belonging to one of the nine neighbouring water molecules (see figure 1.3). To make their results directly comparable with those of other authors, they used the second order correction (2.20) to  $H_{eff}$  to generate an effective BCCF operator of the form (2.27). The choice of a 3s-orbital for the excited state is principally for simplicity, the object of the calculation being simply to estimate whether inter-site processes can be important or not. Excitations to ligands other than the nine water molecules in figure 1.3 are neglected. The full details of the calculation can be found in Christodoulos et al. (1986) and Christodoulos (1987). From now on we will refer to the first reference as 'CEA'.

### 3.2 The Hamiltonian

The Hamiltonian from which their mechanism is derived is

$$H = \sum_i (p_i^2/2m_i) - \sum_n Z_n e^2/|r_i - R_n| + \frac{1}{2} \sum_{i,j} e^2/|r_i - r_j| \quad (3.1)$$

The first term represents the kinetic energy of the electrons in the lattice. The second term represents the electron/nucleus interaction,  $r_i$  being the position vector of the  $i$ th electron,  $R_n$  the position vector of the  $n$ th nucleus in the lattice. The origin of coordinates is taken to be at the centre of the  $Gd^{3+}$  ion, and is labelled  $n=0$ , so that  $R_0 = 0$ . The third term represents the Coulomb interaction between the electrons.

It is convenient at this point to make some simplifying assumptions. In this mechanism we are interested in the excitation of a 4f-electron into an empty neighbouring 3s-orbital and vice-versa. Therefore on second quantizing  $H$ , we are interested in operators of the form  $a^\dagger b$ ,  $b^\dagger a$ ,  $b^\dagger a^\dagger a a$  etc., where  $a^\dagger$  creates a 4f-electron, and  $b^\dagger$  creates an electron in an empty 3s-orbital on an oxygen neighbour. The one-body parts of  $H$  can clearly lead to the  $a^\dagger b$ ,  $b^\dagger a$ , but these can also be obtained from the third term, because on second quantizing it we can get terms of the form  $f_i^\dagger b^\dagger f_j a$  and  $f_i^\dagger b^\dagger a f_j$  (or their hermitian adjoints), in which the excitation is accompanied by the emptying and filling of core states (either on the  $Gd^{3+}$  ion or a neighbouring ligand). Since all core states are assumed to be full at the start, we must have  $i=j$ ,  $f_i^\dagger f_i = 1$ . Therefore these processes lead to effective one-body operators  $b^\dagger a$  and  $a^\dagger b$ . An examination of equations (2.14) shows that such two-body processes are associated with the coulomb interaction (direct and exchange) between the core electrons and the 4f-electrons on the  $Gd^{3+}$  ion. Such processes may be incorporated by defining new effective nuclear charges  $Z_n^e$ , which reflect the fact that the core-electrons tend to shield the 4f-electrons from the full effect of the bare nuclear charges  $Z_n$ . Hence for a  $Gd^{3+}$  ion, which has a total of 54 core electrons,  $Z_0^e = 10$ . The second and third terms of  $H$  then become:

$$- \sum_n Z_n^e e^2/|r_i - R_n| + \frac{1}{2} \sum_{i,j} e^2/|r_i - r_j|$$

In the final term, the prime indicates that we should only include those matrix elements which involve 4f-orbitals alone, or 4f orbitals and empty states on a neighbouring ligand. The second term in H may be simplified as well. CEA have shown that it consists of three important contributions: 1) the attraction of the 4f-electrons to the  $Gd^{3+}$  nucleus (the term for which  $n=0$ ), 2) a large spherical potential energy due to nine effective charges  $Z_{eff}$  (obtained by putting the  $r_i$  equal to zero), and 3) a smaller crystal field term. They argued that contribution 2) will be zero, because the constant PE will appear in matrix elements involving orthogonal basis states. The third term is neglected because it is likely to be small compared with the other terms. Therefore only contribution 1) is retained. The Hamiltonian (3.1) then finally takes the form:

$$H = \sum_i (p^2/2m)_i - \sum_i Z_{eff}^2 e^2/r_i + u \sum_{i \neq j} e^2/|r_i - r_j| \quad (3.2)$$

### 3.3 Perturbation Theory

To obtain an SCCF operator for the inter-site mechanism, CEA used the Method of Stevens. It is therefore necessary to give some consideration to the choice of unperturbed Hamiltonian  $H_0$ , and also to the choice of ground and excited families. The unperturbed Hamiltonian is defined according to equation (2.5) as follows:

$$H_0 = \sum_r E_r P_r \quad (3.3)$$

$$\text{where } E_r = \sum_{n_r} \langle n_r | H | n_r \rangle / \sum_{n_r} \langle n_r | n_r \rangle \quad (3.4)$$

In these expressions,  $|n_r\rangle$  denotes an intermediate coupling state which originates from a given term with fixed values of L and S. The ground family  $P_0$  thus consists of all intermediate coupling states which originate from the  $^4S$  term. Similarly, the next few excited families will consist of those intermediate coupling states which originate from the higher  $^6P, ^6D, ^8I, \dots$  terms. The projection operators  $P_r$  are then given by

$$P_r = \sum_{n_r} |n_r\rangle \langle n_r| \quad (3.5)$$

Much higher up the energy scale, there will be an excited family of states in which an electron has been transferred from the 4f-shell of the Gd<sup>3+</sup> ion to an empty 3s-orbital of an oxygen neighbour.

### 3.4 Contributions to the SCCF

Because the inter-site mechanism involves the excitation and deexcitation of a 4f-electron, it is necessary to use the second order correction to  $H_{eff}$  to obtain an effective operator, i.e.

$$- \sum_{a \neq 0} P_a H P_a / (E_a - E_0) \quad (3.6)$$

To evaluate the mechanism, one must first of all find which terms in  $H$  can lead to an effective operator in (3.6), which, when the angular momentum equivalences (2.16) are used, lead to an SCCF operator of the form (2.27). CEA have found that the following combinations in (3.6) do this:

$$\begin{aligned} (1) & \quad a_1^\dagger b_\alpha : b_\alpha a_1 a_2 a_1 \\ (2) & \quad a_1^\dagger b_\alpha : a_1^\dagger b_\alpha a_2 a_1 \\ (3) & \quad a_1^\dagger a_1 a_2 b_\alpha : b_\alpha a_1 \\ (4) & \quad a_1^\dagger a_1 b_\alpha a_2 : b_\alpha a_1 \\ (5) & \quad a_7^\dagger a_5 a_3 b_\alpha : b_\alpha a_5 a_3 a_1 \\ (6) & \quad a_7^\dagger a_5 a_1 b_\alpha : a_1^\dagger b_\alpha a_2 a_1 \\ (7) & \quad a_7^\dagger a_5 b_\alpha a_1 : b_\alpha a_1 a_2 a_1 \\ (8) & \quad a_7^\dagger a_5 b_\alpha a_1 : a_1^\dagger b_\alpha a_2 a_1 \end{aligned} \quad (3.7)$$

where we have used the labels 1,2,3,5,6,7 for the 4f-electrons, and  $\alpha$  for empty 3s-orbitals on oxygen neighbours. In writing out these processes, we have used a simplified notation. For instance, process number (2) above is shorthand for

$$- P_a a_1^\dagger b_\alpha P_a a_1^\dagger b_\alpha a_2 a_1 P_a / (E_a - E_0)$$

The processes (3.7) can now be simplified to an effective operator acting within the ground family, using the same ideas which were used to reach equation (2.22) in the previous chapter. As an example, consider process

(2). If we follow that discussion, then we see that  $a_3^\dagger b_2 a_2$  must act on a state  $|n_0\rangle$  in the ground family to give a state  $|n_1\rangle$ , belonging to an excited family (say the  $r^{10}$ ), in which a single 4f-electron has been excited to an empty 3a-orbital on an oxygen neighbour.  $a_2^\dagger b_2$  then acts so that, when (3.6) acts on  $|n_1\rangle$ , the result is another state which belongs to the ground family. Process (2) can then be reduced to the following effective operator, acting within the ground family:

$$- 1/\Delta P_2 a_2 b_2 a_3^\dagger b_2 a_2 a_1 P_2 \quad (3.8)$$

In this expression we have put  $\Delta = E_r - E_0$ . Because the 3a-orbital was empty at the start of the process, we must have  $b_2 b_2^\dagger = 1 - b_2^\dagger b_2 = 1$ . Since the  $a$  and  $b$  operators anticommute, (3.8) becomes

$$+ 1/\Delta P_2 a_2 a_3^\dagger a_2 a_1 P_2 \quad (3.9)$$

Up to now, we have neglected to mention the fact that all of the processes in (3.7) are accompanied by a set of appropriate matrix elements, given by equations (2.14). If, for convenience, we define

$$X = p^2/2m - Z e^2/r \quad (3.10)$$

$$U = e^2/2|r_1 - r_2| \quad (3.11)$$

then process (2), when written out in full, becomes

$$+ 1/\Delta \sum_{\alpha} \langle 4f | X | \alpha \rangle \langle 3, \alpha | U | 1, 2 \rangle P_2 a_2^\dagger a_3^\dagger a_2 a_1 P_2 \quad (3.12)$$

where the summation variable  $\alpha$  denotes the set of all relevant quantum numbers.

CEA have performed this reduction down to effective operators acting in the ground family for all of the processes (3.7). We will follow their notation, except that for clarity, we will retain the symbol  $\alpha$  to denote a 3a-orbital on a neighbouring oxygen. The eight reduced contributions are:

$$(1) \quad - 1/\Delta \sum_{\alpha} \langle m_1 | X | \alpha \rangle \langle \alpha, m_3 | U | m_4, m_2 \rangle a_2^\dagger a_1 a_3^\dagger a_2 a_2^\dagger a_2 a_1$$

$$\begin{aligned}
(2) \quad & + 1/\Delta \sum_p \langle m_1 | X | m \rangle \langle m_3, \alpha | U | m_4, m_5 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{3\alpha} \overset{+}{a}_{4\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \\
(3) \quad & - 1/\Delta \sum_p \langle m_1, m_2 | U | \alpha, m_4 \rangle \langle \alpha | X | m_5 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{4\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \\
(4) \quad & + 1/\Delta \sum_p \langle m_1, m_2 | U | m_4, \alpha \rangle \langle \alpha | X | m_5 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{4\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \\
(5) \quad & - 1/\Delta \sum_p \langle m_1, m_2 | U | \alpha, m_4 \rangle \langle \alpha, m_5 | U | m_6, m_7 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{4\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \overset{+}{a}_{7\alpha} \overset{+}{a}_{8\alpha} \\
(6) \quad & + 1/\Delta \sum_p \langle m_1, m_2 | U | \alpha, m_4 \rangle \langle m_5, \alpha | U | m_6, m_7 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{4\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \overset{+}{a}_{7\alpha} \overset{+}{a}_{8\alpha} \\
(7) \quad & + 1/\Delta \sum_t \langle m_1, m_2 | U | m_3, \alpha \rangle \langle \alpha, m_5 | U | m_6, m_7 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{3\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \overset{+}{a}_{7\alpha} \overset{+}{a}_{8\alpha} \\
(8) \quad & - 1/\Delta \sum_t \langle m_1, m_2 | U | m_3, \alpha \rangle \langle m_5, \alpha | U | m_6, m_7 \rangle \overset{+}{a}_{1\alpha} \overset{+}{a}_{2\alpha} \overset{+}{a}_{3\alpha} \overset{+}{a}_{5\alpha} \overset{+}{a}_{6\alpha} \overset{+}{a}_{7\alpha} \overset{+}{a}_{8\alpha}
\end{aligned} \tag{3.13}$$

In these expressions  $|m\rangle$  and  $|\alpha\rangle$  denote 4f-like and 3s-like Wannier functions for  $Gd^{3+}$  and oxygen respectively. We have also defined new summation variables  $p, r, s$  and  $t$ , such that each consists of the set of quantum numbers relevant to the expression for which it is defined. For instance

$$p \equiv \{ m_1, m_2, m_4, m_5, \alpha, \sigma, \sigma' \}$$

The contributions (3.13) are now in a form suitable for the use of the angular momentum equivalences. Notice that they are not all of the same sign; this is a consequence of the fact that the  $a$  and  $b$  operators anti-commute.

### 3.5 Conversion to an Effective Operator

In order to use the angular momentum equivalences (2.16), it is necessary to rearrange the operator products into the form  $a^{\dagger}aa'a$  or  $a^{\dagger}aa'a^{\dagger}a$ . It is interesting to note that there is more than one way of doing this. For instance, consider an operator  $a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}$ . We could then have

$$\begin{aligned}
a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger} &= a^{\dagger}\{a^{\dagger}a - a^{\dagger}a\}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger} \\
&\text{or} \quad - a^{\dagger}\{a^{\dagger}a - a^{\dagger}a\}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}a^{\dagger}
\end{aligned} \tag{3.14}$$

It would therefore seem that the use of the angular momentum equivalences (2.16) will lead to two distinct effective operators. This problem has been examined by Dixon et al. (1984), and they have been able to show that

the two versions in (3.14) will lead to effective operators which are equivalent physically, in the sense that their associated matrix elements are equal. Because CEA were interested in SCCF operators of the form (2.27), they chose the version of (3.14) which leads to this when the angular momentum equivalences are used. One also gets additional terms from the commutation rules which lead to either one-body, purely orbital terms, or two-body terms describing orbit/orbit interactions. It may be shown that the effect of these additional terms is simply to multiply the coefficient  $\mu$  (see equation (3.21)) by 4/3. For further details see either Dixon et al. (1986) or the discussion prior to equation (30) of Christodoulos et al. (1986). The operator string required to get an SCCF operator of the form (2.27) is

$$a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger$$

Therefore if we take process (3) of (3.13), we need to rearrange the operator product  $a^\dagger a^\dagger a e$  into the following form:

$$\begin{aligned} & a_{\sigma\sigma'}^\dagger [a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger - a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger] a_{\sigma\sigma'} \\ &= a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger - a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger a_{\sigma\sigma'}^\dagger \end{aligned} \quad (3.15)$$

When the first term of (3.15) is summed over  $\sigma$  and  $\sigma'$ , and the operator equivalences (2.16) are used, the result is a purely orbital operator. This will have only very small matrix elements within the ground state  $|^8S_{7/2}\rangle$ . This is because  $|^8S_{7/2}\rangle$  is given by [Wybourne 1966]

$$\begin{aligned} |^8S_{7/2}\rangle &= 0.987 |^8S_{7/2}\rangle + 0.162 |^6P_{7/2}\rangle - 0.012 |^6D_{7/2}\rangle \\ &\quad + \text{smaller admixtures} \end{aligned}$$

and the orbital operators have vanishing matrix elements within the  $|^8S\rangle$  and  $|^6P\rangle$  levels, just like the crystal field operators we have already mentioned in earlier chapters. Therefore we need only consider the second term in (3.15). Now CEA have shown that, with a judicious reshuffling of subscripts, processes (1) to (4) in (3.13) give the same contribution. Therefore they may be combined into a single term of the form



$$+ 4/\Delta \sum_p \langle m_1, m_2 | X | \alpha \rangle \langle \alpha, m_3 | U | m_4, m_5 \rangle \overset{\dagger}{a}_{1\alpha} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{3\alpha'} \overset{\dagger}{a}_{4\alpha} \quad (3.16)$$

CEA have also shown that the processes (5) to (8) also lead to the same contribution. They have shown that, after a little algebra, the relevant part which leads to the SCCF operator is

$$- \overset{\dagger}{a}_{1\alpha} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{5\alpha} \overset{\dagger}{a}_{5\alpha'} \overset{\dagger}{a}_{7\alpha'} \quad (3.17)$$

When the sum over  $\alpha''$  is performed in this expression, the result is an SCCF like operator string multiplied by a product which, on using the angular momentum equivalences (2.16), leads to a purely orbital operator. Thus (3.17) becomes

$$- ( \overset{\dagger}{a}_{1\alpha} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{5\alpha} ) \cdot ( \sum_{n1} \Delta a_{5n} \overset{(n)}{O}_{5n-7}(\underline{1}) ) \quad (3.18)$$

The factor  $\Delta a_{5n}$  is given in equation (2.14). Obviously, if (3.18) is to lead to an SCCF operator, we need  $n=0$  and  $m_5 = m_7$ , otherwise we will end up with a three-body operator. Now since  $O_0^0 = 1$ ,  $N_0^0 = 7$  and  $\sum i = 7$  for the 4f-electrons, the last term in (3.18) can be replaced by unity.

When these considerations are applied to processes (5) to (8), they result in the following single term (again after some reshuffling of subscripts):

$$+ 4/\Delta \sum_{\alpha} \langle m_1, m_2 | U | \alpha, m_4 \rangle \langle \alpha, m_5 | U | m_5, m_6 \rangle \overset{\dagger}{a}_{1\alpha} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{2\alpha'} \overset{\dagger}{a}_{5\alpha} \quad (3.19)$$

Where  $\alpha = (m_1, m_2, m_4, m_5, m_6, \alpha, \alpha, \sigma')$ . When the spin summations are carried out, and the angular momentum equivalences (2.16) are applied, the second quantised operators in (3.16) and (3.19) are replaced by the following angular momentum operators:

$$2 \sum_{\alpha\alpha', 1\&J} \Delta a_{1\alpha} \Delta a_{3\alpha'} \overset{(n)}{O}_{1-n}(\underline{1}) \overset{(n')}{O}_{3-n'}(\underline{1}) (1\& + \underline{g}_1 \cdot \underline{g}_1) \quad (3.20a)$$

$$2 \sum_{\alpha\alpha', 1\&J} \Delta a_{1\alpha} \Delta a_{2\alpha'} \overset{(n)}{O}_{1-n}(\underline{1}) \overset{(n')}{O}_{2-n'}(\underline{1}) (1\& + \underline{g}_1 \cdot \underline{g}_1) \quad (3.20b)$$

The SCCF operator which we seek is given by (2.27):

$$\mu \sum_{i \neq j} C_0^i (S_i) S_i \cdot S_j \quad (3.21)$$

and so in equations (3.20) we require either  $n'=2, n=0$  or  $n=2, n'=0$ . In (3.20a) we also require that  $m_1 = m_2, m_3 = m_4$  and in (3.20b) we require  $m_1 = m_4, m_2 = m_3$ . Finally, we need to relate the operator  $C_0^i$  to  $O_0^i$ . To do this, we put  $O_0^i = \lambda C_0^i$  and require that the matrix elements between two 4f-states be identical. With the help of the Wigner-Eckart theorem [Rotenberg et al. 1959], this gives  $\lambda = -22.5$ .

Bearing all of this in mind, the use of equations (3.20a) and (3.20b) in (3.18) and (3.19) then leads to the following expression for  $\mu$ :

$$\mu = \mu_1 + \mu_2 + \mu_3 + \mu_4$$

$$\begin{aligned} \mu_1 &= (-180/\Delta E_0^2 N_2) \sum_r \langle m_1 | X | \alpha \rangle \langle \alpha, m_2 | U | m_3, m_1 \rangle \langle m_1 | O_0^1 | m_1 \rangle \\ \mu_2 &= (-180/\Delta E_0^2 N_2) \sum_r \langle m_1 | X | \alpha \rangle \langle \alpha, m_3 | U | m_2, m_1 \rangle \langle m_2 | O_0^1 | m_2 \rangle \\ \mu_3 &= (-180/\Delta E_0^2 N_2) \sum_r \langle m_1, m_2 | U | \alpha, m_1 \rangle \langle \alpha, m_3 | U | m_2, m_4 \rangle \langle m_2 | O_0^1 | m_2 \rangle \\ \mu_4 &= (-180/\Delta E_0^2 N_2) \sum_r \langle m_1, m_2 | U | \alpha, m_1 \rangle \langle \alpha, m_3 | U | m_2, m_3 \rangle \langle m_3 | O_0^1 | m_3 \rangle \end{aligned} \quad (3.22)$$

In these expressions,  $r = (m_1, m_2, \alpha)$  and  $t = (m_1, m_2, m_3, \alpha)$ . The label  $\alpha$  includes all 3s-orbitals on all nine neighbouring oxygens.

### 3.5 Basis States

In order to evaluate the expressions (3.22), it is necessary to have explicit forms for the basis states representing the 4f-orbitals of  $Gd^{3+}$ , and also for the 3s-like orbitals on the neighbouring oxygens. The Method of Stevens requires that the basis functions used form a complete orthonormal set, for otherwise it is not possible to use the second quantization techniques. Stevens himself suggests that Wannier functions (appendix D) would constitute an appropriate basis set, since they satisfy the completeness and orthonormality requirements. Unfortunately they are awkward to use in numerical calculations, and are rarely used for anything other than formal analysis [Harrison 1980]. However, as Stevens points out, the

low-lying members of a set of Wannier functions localised about a given lattice point will be similar to the corresponding set of atomic orbitals [Stevens 1976 p21]. Therefore CEA made the approximation that the basis functions can be written as atomic orbitals. Strictly speaking, the electrons should be described by basis functions which transform according to the irreducible representations of the point group of the lattice, and not by atomic orbitals, which are more appropriate to the free ion. It is usual to ignore these complications, and assume that basis functions appropriate to spherical symmetry are good enough [Stevens 1976 p24]. The 'correct' basis functions should really be used for accurate numerical work, but as CEA were only interested in a qualitative estimate of the mechanism, they decided to ignore this complication.

The form of the 4f-function which they decided on was:

$$\Psi_{4f}(\underline{r}) = \psi(r) Y_3^m(\theta, \phi) \quad (3.23)$$

where the radial function  $\psi(r)$  is that given by Freeman and Watson (1962):

$$\psi(r) = r^3 \sum_i B_i \exp[-W_i r] \quad (3.24)$$

The values of the  $B_i$  and  $W_i$  are given in table 3.1. The dimensions of the  $W_i$  are  $a_0^{-1}$ , and the dimensions of the  $B_i$  are  $a_0^{-3/2}$ .

| Table 3.1: $B_i$ and $W_i$ for $Gd^{3+}$ |           |        |
|--|-----------|--------|
| i  | $B_i$     | $W_i$  |
| 1  | 1923.8151 | 12.554 |
| 2  | 329.6672  | 7.046  |
| 3  | 43.2748   | 4.697  |
| 4  | 1.5047    | 2.578  |

The choice of the neighbouring 3s-orbital is not so clear cut. CEA decided that the most realistic choice would be one of hydrogenic form:

$$\Psi_{3a}(r') = A(4A)^{3/2} [1 - 2Ar' + (8/3)(Ar')^2] \exp(-Ar') Y_0^0 \quad (3.25)$$

In this expression,  $r'$  denotes the radial variable defined with respect to an origin at the centre of the corresponding oxygen,  $A$  is a parameter, and  $Y_0^0$  is the spherical harmonic appropriate to an s-state wavefunction. The expression is normalized for all  $A > 0$ . In order to determine the parameter  $A$ , CEA decided to try and make  $\Psi_{3a}$  as orthogonal as possible to the  $1s$ - and  $2s$ -oxygen wavefunctions of Clementi and Roetti (1974). The result is a value of  $A$  lying between  $A = 1.6$  and  $A = 1.7$ , with the minimum occurring at  $A = 1.67$ . Unfortunately, the  $3s$ -orbitals chosen in this way are not orthogonal to the  $4f$ -functions in (3.23) and (3.24). This is because although the spherical harmonics are different, the functions are centred on different sites. In order to make the  $4f$ - and  $3s$ -wavefunctions orthogonal, CEA used the procedure of Löwdin (1950), which is useful if the overlaps between the non-orthogonal functions are small. The procedure results in new 'orthogonalized'  $4f$ - and  $3s$ -orbitals, given by

$$\tilde{\psi}_{4fm} = \psi_{4fm} - \frac{1}{2} \sum_R S_{4m} \psi_{3aR} \quad (3.26a)$$

$$\tilde{\psi}_{3aR} = \psi_{3aR} - \frac{1}{2} \sum_{m'} S_{3aR} \psi_{4fm'} - \frac{1}{2} \sum_m S_{4m} \psi_{4fm} \quad (3.26b)$$

where  $\tilde{\psi}_{3aR}$  and  $\tilde{\psi}_{4fm}$  are the new orthogonalized orbitals,  $\psi_{4fm}$  is the wavefunction (3.23), and  $\psi_{3aR}$  is the wavefunction (3.25) centred on an oxygen ion at position vector  $R$ . The quantities  $S_{4m}$  and  $S_{3aR}$  are the overlaps  $\langle \psi_{4fm} | \psi_{3aR} \rangle$  and  $\langle \psi_{3aR} | \psi_{3aR'} \rangle$  respectively.

### 3.7 The Result

The only quantity which needs to be evaluated now is the energy denominator  $\Delta$ . This is essentially the energy difference between the ground state configuration  $4f^7$  and the excited configuration  $4f^6 3s$ . CEA have estimated this quantity by considering the difference between the energy of a  $4f$ -electron and an electron in the  $3s$ -orbital, making due allowance for the effect of the large positive charge of the  $Gd^{3+}$  ion. We will not elaborate further on their calculation, for another method of calculating  $\Delta$  will be given later in this thesis.

It is useful to know precisely what value of  $\mu$  is required to obtain agreement with experiment. The analysis of Tuszyński et.al. (1984,1986) leads to a value of  $\mu$  (call it  $\mu_{ex}$ ) of  $148.3 \text{ cm}^{-1}$ , which is found to give a ZFS of  $+0.853 \text{ cm}^{-1}$ . So we may write, following CEA,  $\mu_{ex} = 0.853$ , where  $\mu$  is obtained by finding the matrix elements of the SCCF within the ground family of  $|^8S_{7/2}\rangle$  states [Dixon and Chatterjee 1980]. Let the contribution from the mechanism of CEA be  $\mu_{eff}$ . Therefore from (1.10) and (1.12) we must have

$$\begin{aligned} \mu(\mu_{ex} + \mu_{eff}) - 0.432 &= 0.236 \text{ cm}^{-1} \\ \mu_{eff} &= -32.16 \text{ cm}^{-1}. \end{aligned}$$

Therefore, to get agreement with experiment, all further mechanisms must give a contribution of  $\mu = -32.16 \text{ cm}^{-1}$  to the SCCF coefficient in (3.21).

The results of CEA are given in table 3.2 below: [Christodoulos, 1987]

| $A$ | $Z_{eff}=0.0$ | $Z_{eff}=3.0$ | $Z_{eff}=3.5$ | $Z_{eff}=4.0$ |
|-----|---------------|---------------|---------------|---------------|
| 1.4 | -3.43         | -9.85         | -14.32        | -20.21        |
| 1.5 | -14.42        | -34.84        | -45.60        | -65.98        |
| 1.6 | -11.78        | -24.97        | -30.70        | -39.83        |
| 1.7 | -0.30         | -0.58         | -0.69         | -0.83         |

In this table,  $Z_{eff}$  is the charge felt by an electron centred on an oxygen atom due to the presence of the  $\text{Gd}^{3+}$  ion. It appears as a consequence of the way that CEA obtained  $A$ . Clearly one would expect  $Z_{eff} = 3$ . All units are in  $\text{cm}^{-1}$ . A glance at these results indicates that a value of  $\mu_{eff}$  of the required sign and order of magnitude is obtained for  $Z_{eff}$  between about 3.0 and 3.5, and for  $1.6 < A < 1.7$ , i.e. that range of  $A$  for which the  $3a$ -orbital is most nearly orthogonal to the  $1s$ - and  $2a$ -atomic wave-functions on the same site. It would therefore seem reasonable to conclude

that off-site processes can lead to important contributions to the ZFS of  $Gd^{3+}$  in an ethylsulphate host lattice.

### 3.6 Summary and Discussion

In this chapter we have presented a concrete example to demonstrate how the Method of Stevens works in practice. A very important example it has proved to be too, for the demonstration that inter-site processes can lead to significant contributions to the SCCF coefficient has led to a big step forward in our understanding of the zero field splitting in S-state ions.

However, as CEA point out, a calculation of this nature can only really give qualitative results, for the problem contains many uncertainties. For instance, it is difficult to tell whether the  $3s$ -orbital (3.25) is a good choice or not without doing a molecular orbital type calculation for the  $GdES$  complex. The calculation of the energy denominator  $\Delta$  is also subject to some uncertainties, but we will attempt to make a more accurate estimate of  $\Delta$  later on in the thesis. Another approximation of unknown validity is the neglecting of the ethylsulphate radicals. The safest conclusion to be drawn from the results of this chapter is that inter-site processes play an important role in determining the ZFS of  $Gd^{3+}$  in the ethylsulphate host.

Finally, it is worth reminding ourselves of how CEA made the basis states mutually orthogonal. They chose the parameter  $A$  so that (3.25) was as close as possible to being orthogonal to the  $1s$ - and  $2s$ -states, and they made (3.25) orthogonal to the  $4f$ -states using the procedure of Löwdin. It is worth noting in passing that the use of the orthogonalized orbitals (3.26) in equations (3.22) leads to a considerable increase in the algebraic complexity of the problem.

## CHAPTER 4

### The Method of Stevens in a Dynamic Lattice

#### 4.1 Introduction

In the previous chapter we saw that the inter-site mechanism of CEA can produce a contribution to the ZFS of  $Gd^{3+}$  which, when added to the mechanisms of chapters two and one, leads to a marked improvement in comparison with the experimental result. However, there are other factors to be considered, for although the mechanism yields a substantial contribution to the ZFS, a glance at table 3.2 would seem to indicate that it is not sufficient to give complete agreement. (In view of the comments at the end of the previous chapter, it is not possible to assign a single value to  $\mu_{eff}$  with any degree of confidence. However what we can do is look at the columns for  $Z_{eff} = 3.0$  and  $3.5$ , and the rows for  $A = 1.6$  and  $1.7$ , and from the results infer that  $\mu_{eff}$  is of the required sign, but a bit too small).

From this chapter onwards, we will be concerned with a new source of contributions to the zero field splitting. All mechanisms so far have been calculated with the tacit assumption that the lattice is stationary. If the lattice is at a finite temperature, the ligands will not be stationary, but will oscillate about their equilibrium positions. Our objective will be to try and estimate the extent of the influence of lattice vibrations, and this will be done by estimating how much the inter-site mechanism of CEA is changed when the ligands are allowed to vibrate. To do this we will use the Method of Stevens, which has to be modified slightly to take account of the motion of the ligands. The modifications which have to be made will be the subject of most of this chapter, but first, given that lattice vibrations can have important consequences in crystal field phenomena, it has seemed appropriate to give a brief discussion of why they are important.

## 4.2 Orbit-Lattice Interactions

In order to measure experimentally the lowest energy levels of a paramagnetic ion in a crystal, a technique known as electron spin resonance (ESR) is employed. Put simply, ESR involves applying a static magnetic field to the crystal, causing a Zeeman splitting of the levels. Transitions between these levels are then induced using a small RF field [Taylor and Darby, 1972]. The result is a set of absorption lines, at frequencies corresponding to the allowed transitions within the energy level scheme. Now the Uncertainty Principle tells us that for the absorption lines to be sharp, the lifetime of the excited states should be long. A measure of the sharpness is provided by a quantity known as the 'spin-lattice relaxation time'  $\tau$ , which is inversely proportional to the probability of a transition between two levels in the crystal. So if  $\tau$  is long, one expects sharp lines; if  $\tau$  is short, one would expect broader lines. The magnitude of  $\tau$  is determined by the strength of the orbit-lattice interaction; that is, the strength of the coupling between the paramagnetic ion and the lattice vibrations. This situation has been investigated by Orbach (1961) and Stevens (1967), who both showed that the orbit-lattice interaction arises as a result of the fact that if the lattice is vibrating, the paramagnetic ion feels a crystal field which is changing with time. The Hamiltonian for the orbit-lattice interaction is then equal to the difference between the total crystal field at the ion and the crystal field which would be felt if the lattice were stationary. For S-state ions like  $Gd^{3+}$ , orbit-lattice interactions are generally weak because they have no orbital angular momentum in their ground states, and so spin-lattice relaxation times are expected to be long. This is found to be the case, and as a consequence one can usually observe sharp lines in S-state ions, even at room temperature (Dieke 1968).

The sharpness of the spectral lines of S-state ions in insulating crystals means that it is possible to observe another interesting effect. As the temperature is changed, it is found that the zero field splitting changes too. The variation with temperature of the zero field splitting of the ground state of  $Gd^{3+}$  in  $GdES$  is given in table 4.1. The data is taken from Dagg et al. (1969), and as usual all splittings are in units of  $cm^{-1}$ . In



non S-state ions, increasing the temperature results in a broadening of the lines, because for these ions  $\chi$  decreases rapidly with temperature. ESR is then possible only at low temperatures [Orbach and Blume, 1961].

Table 4.1: temperature dependence of ZFS for  $Gd^{3+}$  in GdES

| T/K   | $M_J = \frac{7}{2}$<br>$\rightarrow \frac{5}{2}$ | $M_J = \frac{5}{2}$<br>$\rightarrow \frac{3}{2}$ | $M_J = \frac{3}{2}$<br>$\rightarrow \frac{1}{2}$ | $M_J = \frac{1}{2}$<br>$\rightarrow -\frac{1}{2}$ |
|-------|--|--|--|---|
| 4.2   | 0.1128   | 0.0834   | 0.0455   | 0.2417  |
| 53.0  | 0.1141   | 0.0843   | 0.0461   | 0.2445  |
| 77.0  | 0.1149   | 0.0852   | 0.0464   | 0.2465  |
| 90.0  | 0.1153   | 0.0851   | 0.0465   | 0.2469  |
| 130.0 | 0.1158   | 0.0856   | 0.0469   | 0.2483  |
| 285.0 | 0.1101   | 0.0816   | 0.0449   | 0.2386  |

Many authors have attempted to calculate the extent of the splitting induced by the (weak) orbit-lattice interaction. Huang (1967) and Menne (1968) both attempted this calculation for  $Gd^{3+}$  in  $CaF_2$  at 293K, but unfortunately their results are not comparable; Huang concludes that contributions from the orbit-lattice interaction are important, Menne concludes that they are not. Both authors based their calculations on an expression for the orbit-lattice interaction first obtained by Van-Vleck (1940), and both were careful to use intermediate coupling wavefunctions for the ground state of  $Gd^{3+}$ .

Finally in this section on orbit-lattice interactions, we must mention the Jahn-Teller effect. If the ground state of an ion in a crystal contains some orbital electronic degeneracy, then it was shown by Jahn and Teller (1937) and Jahn (1938) that the system would be unstable against displacements of the neighbouring atoms. The exceptions to this rule are linear molecules. The Jahn Teller effect has been the subject of much research effort over the years, and it is not really possible to provide a brief overview of the subject here. For a comprehensive introduction to the Jahn Teller effect, the reader should see the review article by Bates (1978).

For the rest of the thesis we will be attempting to estimate the contribution of lattice vibrations to the zero field splitting of  $Gd^{3+}$ , not by using the Van-Vleck orbit-lattice interaction, but by using the Method of Stevens to estimate how much the mechanism of CEA is changed when the neighbouring water molecules are made to vibrate. The results in table 4.1 should provide a guide as to whether this idea is plausible or not. First of all though, we must consider how the Method of Stevens should be modified for use in a lattice where lattice vibrations are present. We will refer to such a lattice as a 'dynamic lattice'. A lattice in which the nuclei are taken to be stationary will be referred to as a 'static lattice'.

#### 4.3 Many-Electron States in the Dynamic Lattice

In section 2.3 of chapter 2 we defined the unperturbed Hamiltonian for a static lattice, and in doing so a great deal of attention was paid to the problem of ensuring that the many-electron states  $|n\rangle$  were good approximations to the true crystal wavefunctions. This then ensures that the unperturbed Hamiltonian  $H_0$  is a good approximation to the full Hamiltonian  $H$ . The definition (2.5) also exploits the fact that the states  $|n\rangle$  may be separated into families, so that  $H_0$  can be constructed in such a way that it consists of sequences of well spaced, degenerate levels. In moving to a dynamic lattice, it would be desirable to retain these characteristics of  $H_0$ . Therefore let us begin by examining the form of the many-electron states in the dynamic lattice. The true crystal wavefunctions will be the eigenfunctions of the following Hamiltonian:

$$H_0(\underline{r}, \underline{R}) = T(\underline{R}) + U(\underline{R}) + H_0(\underline{r}) + H_{el}(\underline{r}, \underline{R}) \quad (4.1)$$

where  $T(\underline{R})$  is the kinetic energy of the nuclei,  $U(\underline{R})$  is the electrostatic interaction between the nuclei,  $H_0(\underline{r})$  is the electron kinetic energy plus the electron/electron interaction, and  $H_{el}(\underline{r}, \underline{R})$  is the interaction between the electrons and the nuclei. The variable  $\underline{r}$  represents the set of all electronic coordinates, and  $\underline{R}$  is the set of all nuclear coordinates. The solution of (4.1) is not possible without the help of some approximations. Therefore we will assume that the adiabatic approximation (AA) is valid.

The following treatment of (4.1) using the AA is based on that given in the excellent book by Horton and Maradudin (1974). Because the kinetic energy of the nuclei is small compared with that of the electrons, owing to their much larger masses, it is usual in the AA to treat  $T(R)$  as a perturbation on the rest of the Hamiltonian. Therefore an unperturbed Hamiltonian is defined as follows:

$$H_0(r, R) = U(R) + H_e(r) + H_{el}(r, R) \quad (4.2)$$

The eigenfunctions and eigenstates of (4.2) are assumed to be known:

$$H_0 \phi_n(r, R) = E_n(R) \phi_n(r, R) \quad (4.3)$$

Here  $n$  is a quantum number which represents the electronic state of the crystal. The nuclear coordinates  $R$  act as parameters for the eigenvalues and eigenstates. Note in particular that if the nuclei are fixed in their equilibrium positions, then (4.2) coincides with (2.1) if we put  $U(R_0)=0$ , where  $R_0$  represents the set of equilibrium coordinates of the nuclei. Our problem now is to solve the exact Schrodinger equation

$$H \Psi(r, R) = E \Psi(r, R) \quad (4.4)$$

In the AA it is assumed that the exact states  $\Psi$  can be expanded in terms of the unperturbed states  $\phi$  as follows:

$$\Psi(r, R) = \sum_u C_u(u) \phi_n(r, R) \quad (4.5)$$

In this expression,  $u$  denotes the set of nuclear displacements, and is given by

$$R - R_0 = xu,$$

where  $x$  is the expansion parameter for the perturbation theory. It may be shown [Horton and Maradudin pp 4-5] that  $x = (m/M)^{1/2}$ , where  $m$  is the mass of an electron and  $M$  is the mass of a nucleus, if the harmonic approxi-

ation of lattice vibrations is to be a direct consequence of the AA.  $\zeta_n(u)$  is a vibrational wavefunction to be determined.

The perturbation theory then leads to the following expression for  $\Psi$ :

$$\Psi_{nv}(r, u) = \zeta_{nv}(u) \Phi_n(r, R), \quad (4.6)$$

subject to the following conditions:

- 1) The vibrational wavefunction  $\zeta_{nv}(u)$  is determined solely by the properties of the  $n$ th electronic state.
- 2) The nuclear motion does not induce any electronic transitions.

In (4.6),  $v$  is a vibrational quantum number. The wavefunction  $\Psi_{nv}$  in (4.6) now has a simple interpretation. The first term describes the motion of the nuclei, and the second term then shows that the electrons move as if the nuclei were fixed in their instantaneous positions  $R$ . The effective potential for the nuclear motion is derived from the energy eigenvalue  $E_n(R)$  in (4.3).

By choosing  $x = (m/M)^{1/2}$ , it may be shown that the harmonic approximation for the lattice vibrations emerges from the perturbation theory in a simple way [Horton and Maredudin p51]. In this approximation it may be shown that the wavefunction (4.6) takes the form

$$\Psi_{nv}(r, y) = \zeta_{nv}(y) \Phi_n(r, R_n) \quad (4.7)$$

That is, the electronic wavefunction is that which would be obtained if the nuclei were nailed down in their equilibrium positions. The nuclear motion is now determined from the equation

$$H_b \zeta_{nv} = E_{nv} \zeta_{nv} \quad (4.8)$$

where  $H_b$  is the sum of the kinetic and potential energies of the nuclei in the harmonic approximation.

The reader may feel that the use of the adiabatic approximation is not justified in the context of the Method of Stevens, for it may be shown that it is only valid if the separation of the electronic energies is much greater than the vibrational energies [Bersuker 1984]. As we mentioned in chapter two, the many-electron states  $|n\rangle$  will in general be pseudo-degenerate, and so the introduction of lattice vibrations can be expected to produce a considerable amount of mixing of these states. This in fact is not a problem, for as we shall see later, it is not possible to include any phenomena involving lattice vibrations in the unperturbed Hamiltonian. These effects, and others which involve a breakdown of the adiabatic approximation, will then emerge from the perturbation theory.

The point of going through this analysis with the AA is that  $\Phi_n(\underline{r}, R_n)$  is a solution of (4.2) with  $R \equiv R_n$ . If we put the factor  $U(R_n)$  in (4.2) equal to zero for convenience, then we see that  $H_n(\underline{r}, R_n)$  is in fact identical to the Hamiltonian (2.1) for the static lattice. Therefore we can see that the  $\Phi_n(\underline{r}, R_n)$  are the many-electron states to which Stevens was trying to approximate in his theory for the static lattice. The state (4.7) is then an approximate solution of (4.1) in the AA.

The vibrational wavefunction  $\zeta_{\nu}$  is determined from equation (4.8). It is well known that the vibrational Hamiltonian  $H_{\nu}$  may be reduced to a diagonal form, in the harmonic approximation, by rewriting it in terms of the normal coordinates of the lattice. When the normal coordinates are second quantized,  $H_{\nu}$  takes the following form [Reissland 1972]:

$$H_{\nu} = \sum_{\mathbf{g}j} \hbar \omega(\mathbf{g}j) [ \alpha_{\mathbf{g}j}^{\dagger} \alpha_{\mathbf{g}j} + \frac{1}{2} ] \quad (4.9)$$

where  $\alpha_{\mathbf{g}j}^{\dagger}$  creates a phonon of wavevector  $\mathbf{g}$ , belonging to the  $j^{\text{th}}$  branch, and  $\omega(\mathbf{g}j)$  is the dispersion relation for the phonons. The eigenstates of  $H_{\nu}$  may be written in the form  $|Q\rangle$ , where  $Q$  represents the occupation numbers of the various phonon states, i.e.

$$|Q\rangle \equiv | n(\mathbf{g}_1j_1) \dots n(\mathbf{g}_nj_n) \dots n(\mathbf{g}_1j_r) \dots n(\mathbf{g}_nj_r) \rangle,$$

where the crystal lattice is assumed to contain  $n$  unit cells and  $r$  basis atoms per unit cell.

Therefore, within the AA, the true crystal wavefunctions may be written in the following approximate form:

$$\Psi_{av}(\underline{r}, \underline{y}) = \zeta_{av}(\underline{y}) \Phi_n(\underline{r}, \underline{R}_n) \quad (4.10)$$

From (4.10) we can see that the vibrational wavefunction  $\zeta$  depends on the electronic quantum number  $m$ . This is because the potential energy function for the nuclear motion is derived from the eigenvalue  $E_m(\underline{R})$  in (4.3). The potential energy for the nuclear motion is usually written in terms of a set of empirical force constants, which reflect the strength of the bonding between pairs of ions in the crystal. The number of force constants required may be determined from a knowledge of the point group of the lattice, and their values may be obtained from observations of vibrational spectra (Wilson et.al, 1980).

#### 4.4 The Unperturbed Hamiltonian

In the formulation of the Method of Stevens for the static lattice, the unperturbed Hamiltonian was defined so that its eigenstates were the states  $|n_r\rangle$ , equal to linear combinations of Slater determinants formed from appropriate Wannier functions. In a similar way, we would like the unperturbed Hamiltonian for the dynamic lattice to have eigenstates which are good approximations to the states (4.10). We have already shown that the electronic wavefunction  $\Phi_n(\underline{r}, \underline{R}_n)$  is the wavefunction to which Stevens was trying to approximate when he formed the states  $|n_r\rangle$ . Therefore let us define a similar set of states  $|N_r\rangle$  for the dynamic lattice, as follows:

$$|N_r\rangle = |n_r\rangle |Q\rangle \quad (4.11)$$

Note that this definition allows us to retain the concept of a family of states. This is a consequence of employing the AA in the derivation of (4.10), so that the total wavefunction (4.10) becomes a simple product of lattice and electronic wavefunctions. In the same spirit as equations

(2.5) to (2.7), let us define the following unperturbed Hamiltonian for the dynamic lattice:

$$H_0^D = \sum_r E_r^D P_r^D \quad (4.12)$$

$$\text{where } E_r^D = \sum_{N_r} \langle N_r | H_d | N_r \rangle / \sum_{N_r} \langle N_r | N_r \rangle \quad (4.13)$$

$$\text{and } P_r^D = \sum_{N_r} |N_r\rangle \langle N_r| \quad (4.14)$$

Whilst this definition seems to be a logical extension of the ideas of chapter two, it has one serious flaw. This  $H_0^D$  will probably contain terms which refer to lattice vibrations, or terms which couple the electronic states with the lattice. Since lattice vibrations are associated with a continuum of levels, (4.12) is most unlikely to consist of a set of well spaced, degenerate levels. Therefore it cannot be considered a good choice for the unperturbed Hamiltonian [Sigmund and Stevens 1968]. It is therefore necessary to relegate all terms involving lattice vibrations to the perturbation. The easiest way to do this is to write (4.1) in the form

$$H_d = H_{el} + H_{ph} + H_{e/p} \quad (4.15)$$

where  $H_{el}$  is composed of all of the purely electronic operators,  $H_{ph}$  is composed of purely phonon operators, and  $H_{e/p}$  contains the electron/phonon interactions. These originate from the interaction between the electrons and the nuclei, written in the form

$$\begin{aligned} H_{e/p} &= - \sum_n Z_n e^2 / |\underline{r}_1 - \underline{R}_{en} + \underline{u}_n| \\ &= - \sum_n Z_n e^2 / |\underline{r}_1 - \underline{R}_{en}| - \sum_n Z_n e^2 \underline{u}_n \cdot \nabla_n (1/|\underline{r}_1 - \underline{R}_{en}|) \end{aligned} \quad (4.16)$$

where  $\underline{R}_{en}$  is the equilibrium position of the  $n^{\text{th}}$  nucleus, and it is to be understood that the second term is evaluated at the equilibrium coordinates of the  $n^{\text{th}}$  nucleus. The first term in (4.16) contributes to  $H_{el}$ , and the second gives the electron/phonon interaction. It is now seen that  $H_{el}$  is equal to the full Hamiltonian (2.1) for the static lattice. In view of this, let us modify our definition of the unperturbed Hamiltonian to

$$H_0^0 = \sum_r E_r^0 P_r^0 \quad (4.17)$$

$$\text{where } E_r^0 = \sum_{|Q\rangle} \langle N_r | H_0 | N_r \rangle / \sum_{|Q\rangle} \langle N_r | N_r \rangle = E_r \quad (4.18)$$

$$\text{and } P_r^0 = \sum_{|Q\rangle} |N_r\rangle \langle N_r| = P_r \cdot I_{ph} \quad (4.19)$$

where  $P_r$  and  $E_r$  are the projection operators and energy eigenvalues of the unperturbed Hamiltonian for the static lattice. The last step of (4.18) follows from the orthonormality of the phonon wavefunctions  $|Q\rangle$ , and in (4.19)  $I_{ph}$  is the identity operator within the subspace of phonon states. (4.17) is now almost identical to the unperturbed Hamiltonian for the static lattice, except for the fact that the projection operators are multiplied by the unit operator in the phonon subspace. It consists of a sequence of well spaced, degenerate levels, with the states  $|N_r\rangle$  as eigenstates, and the  $E_r$  as the corresponding eigenvalues. Note in particular that  $H_0^0$  has the same symmetry properties as the unperturbed Hamiltonian for the static lattice. The results (4.17) to (4.19) are precisely the same as those obtained by Sigmund and Stevens (1988), who were using the Method of Stevens to investigate some of the properties of high temperature superconductors.

#### 4.5 Perturbation Theory in the Dynamic Lattice

Having seen that the unperturbed Hamiltonian (4.17) is almost identical to that for a static lattice, it might well be thought that the perturbation theory can be carried out in a similar manner, and that we will end up with the same effective operator as that in chapter two. Unfortunately this is not quite the case. The problem stems from the fact that we need to include the lattice vibrations in the perturbation, having excluded them from the unperturbed part. As Sigmund and Stevens (1988) point out, the version of the perturbation theory given in chapter two is actually based on a treatment given by Messiah (1963), which discusses a Hamiltonian  $H_0 + \lambda V$ , where  $\lambda$  is varied from 0 to 1. In this treatment the assumption is made that for an infinitesimally small  $\lambda$ , the states belonging to the ground family do not overlap with those from excited families. When lattice vibrations are introduced into  $V$ , this condition is unlikely to be



satisfied, because of the continuum nature of the phonon energy levels. Therefore the perturbation scheme of chapter two is not valid.

Fortunately there is another version of the perturbation theory, due to Bloch (1959), which avoids this assumption. In this version the effective operator takes the form

$$H_{eff} = P_0 V U, \quad (4.20)$$

$$\text{where } U = (E_0 - H_0)^{-1} (1 - P_0) (V - UV) U$$

and  $U = P_0$  when  $V = 0$ . From (4.20), the effective operator is found to be

$$H_{eff} = P_0 V P_0 - \sum_{n \neq 0} P_0 V P_n V P_n / (E_0 - E_n) \quad (4.21)$$

to second order. It is interesting to note that this is precisely the same effective operator that was obtained for the static lattice, although it may differ in the higher order corrections. So for the dynamic lattice, the effective operator finally takes the form

$$H_{eff} = P_0^2 H_0 P_0^2 - \sum_{n \neq 0} P_0^2 H_0 P_n^2 H_0 P_n^2 / (E_0 - E_n) \quad (4.22)$$

where we have put  $V = H_0 - H_0^2$ . The projection operators are given in (4.10). Note that the energy denominator in the second term is the same as that for the static lattice. This effective operator plays the same role as that for the static lattice, except that the electronic operators will now be multiplied by products of phonon operators. On performing a thermal average over all phonon modes, the result will be an effective electronic operator multiplied by a temperature dependent factor.

#### 4.6 Basis States in the Dynamic Lattice

Because the Method of Stevens relies on the use of second quantization techniques, it is necessary to consider the problem of basis functions in the dynamic lattice. Let us suppose that we already have a complete orthonormal set of basis functions for the static lattice (i.e. the Wannier

functions), with each function centred on a particular nucleus. When the nuclei start to vibrate, it is reasonable to assume that the basis functions will move so as to stay centred on their respective nuclei. However, if the basis functions are to remain complete and orthonormal, it follows that they must not only move with the nuclei, they must also change their shapes in an appropriate way. This problem has been examined by Stevens (1973), and he has shown that the answer lies in the use of a unitary transformation  $\exp(-iS)$ . Suppose that  $\phi_n$  is a member of the original set of functions. We can define a new function

$$\theta_n = \exp(-iS) \phi_n \quad (4.23)$$

$$\text{where } S = (1/2\hbar) \sum_i \{ P(R_{ni}) \hat{p}_i \hat{R}_{ni} + \hat{p}_i \hat{R}_{ni} P(R_{ni}) \} \quad (4.24)$$

In (4.24),  $\hat{p}$  is the momentum operator,  $\hat{R}_{ni}$  is the displacement of the  $n^{\text{th}}$  nucleus (from now on we will denote the displacements of nuclei from their equilibrium positions by  $\hat{R}$  instead of  $\underline{u}$ ), and  $P(R_{ni})$  is the projection operator for all basis functions centred on the  $n^{\text{th}}$  nucleus.

Since  $P(R_{ni})$  gives non-zero contributions only when it operates on a function on the  $n^{\text{th}}$  nucleus, we find that for small displacements

$$\begin{aligned} \langle \theta_n(R_n) | \theta_n(R_n) \rangle &= \langle \phi_n(R_n) | \exp(-iS) | \phi_n(R_n) \rangle \\ &= \langle \phi_n(R_n) | 1 - i\hat{R}_{ni} \cdot \nabla | \phi_n(R_n) \rangle \\ &= \langle \phi_n(R_n) | \phi_n(R_n - \hat{R}_{ni}) \rangle \end{aligned}$$

So the effect of  $\exp(-iS)$ , at least to first order in displacements, is to displace the function  $\phi_n(R_n)$  through an amount  $\hat{R}_{ni}$ . When  $\exp(-iS)$  is expanded to higher orders in  $\hat{R}_{ni}$ , the effect is to change  $\phi_n(R_n)$  as well as to displace it.

The most important property of the transformation follows from (4.23)

$$\langle \theta_n(R_n) | \theta_n(R_n) \rangle = \langle \phi_n(R_n) | \phi_n(R_n) \rangle \quad (4.25)$$

Therefore if the basis set consisting of the  $\phi_n$  forms an orthonormal set, so does the basis set consisting of the  $\Phi_n$ . The completeness of this new basis set follows from the unitarity of the transformation  $\exp(-iS)$ , and from the fact that the  $\phi_n$  are assumed to form a complete set.

Compared with the ideas of chapter two, there seems to be a slight inconsistency in the ideas of this chapter. The second quantized operators for the dynamic lattice will now create and annihilate electrons in the states (4.23). It would therefore be expected that a many-electron state, formed from the application of strings of these operators on the vacuum state, would have the following form:

$$|N_r\rangle = \exp(-iS) |n_r\rangle \quad (4.26)$$

$$\text{where } S = \sum_j S_j \quad (4.27)$$

The sum in (4.27) is over all electrons, the subscript  $j$  indicating that the coordinates of the  $j^{\text{th}}$  electron have been substituted into (4.23). With this choice of many-electron state, the unperturbed Hamiltonian would be as follows [Stevens 1973]:

$$H_0^0 = \sum_r E_r^0 P_r^0 \quad (4.28)$$

$$\text{where } E_r^0 = \sum_{n_r} \langle n_r | \exp(iS) H_0 \exp(-iS) | n_r \rangle / \sum_{n_r} \langle n_r | n_r \rangle \quad (4.29)$$

$$\text{and } P_r^0 = \sum_{n_r} \exp(-iS) | n_r \rangle \langle n_r | \exp(iS) \quad (4.30)$$

This Hamiltonian has the advantage that it will certainly contain all of the interactions within the dynamic lattice, but this almost certainly means that it will not have eigenstates which fall into well spaced, degenerate levels, which is a prerequisite for the perturbation theory to be valid. Also, the algebraic manipulation of these equations would pose a formidable problem. The justification for the use of the states (4.11) is that they are simple approximations to the states (4.26), within the confines of the adiabatic approximation. Since (4.11) leads to an unperturbed

Hamiltonian and a perturbation theory with more convenient properties than (4.28)-(4.30), it must be considered a better starting point than (4.26).

Finally we note that the same notation may be used for the second quantized operators in the dynamic lattice, provided that a state in the static lattice with a given set of quantum numbers can still be described by the same quantum numbers when the nuclei begin to vibrate. It then follows that the angular momentum equivalences (2.16) are valid in the dynamic lattice.

#### 4.7 Summary and Discussion

In this chapter we have developed a scheme whereby the Method of Stevens can be used for a dynamic lattice. In doing so we have reproduced some of the results of Sigmund and Stevens (1988). The two most important factors which must be borne in mind in moving from a static lattice to a dynamic lattice are 1) the unperturbed Hamiltonian should have a sequence of well spaced, degenerate levels, and 2) the basis functions used in the second quantisation formalism must remain mutually orthonormal. As we mentioned at the end of the last section, the choice of basis functions (4.23) leads to many electron states which, when they are used in the definition of the unperturbed Hamiltonian, are unlikely to lead to a perturbation scheme which satisfies criterion 1). Therefore the adiabatic approximation is used to rewrite the many-electron states as simple products of electronic and lattice wavefunctions. This then leads to a more useful formalism. Unfortunately, it is then necessary to relegate all terms involving lattice vibrations to the perturbation. These, and the various orbit-lattice interactions, can then be expected to emerge from the various orders of perturbation theory.

## CHAPTER 5

### Formulation of the Problem

#### 5.1 Introduction

We are now, at last, in a position to begin the calculation of our mechanism. In chapter three we discussed the calculation of the inter-site mechanism for the static lattice, and in chapter four we discussed the modifications which have to be made to the Method of Stevens for use in a dynamic lattice. Our mechanism is obtained by reformulating the ideas of chapter three within the framework of the results of chapter four.

In this chapter, we will set up the problem. Firstly we will discuss in more detail the Hamiltonian for our mechanism in a dynamic lattice, and this will provide an opportunity to elaborate a little further on the properties of the effective operator (4.22). In section 5.3 we will discuss the assumptions and approximations which are made in the calculation. By the end of the chapter it will be clear to the reader that the evaluation of the mechanism is a rather lengthy process, and so unfortunately some approximations are necessary to make the calculation tractable. In section 5.4 we will obtain an analytical expression for the magnitude of the effective SCCF operator generated by the mechanism, and in section 5.5 we will discuss the evaluation of the matrix elements which appear, within the basis states (4.23). In section 5.6 we will use the results of sections 5.4 and 5.5 to derive an expression for the magnitude of the SCCF in terms of matrix elements in the static lattice, and within the harmonic approximation for the lattice vibrations.

#### 5.2 The Hamiltonian for the Dynamic Lattice

The Hamiltonian from which the mechanism is to be derived is given by

$$\begin{aligned} H_0 = & \sum_i (p_i^2/2m)_i + \frac{1}{2} \sum_{i,j} e^2/|r_i - r_j| - \sum_{a1} Z_a e^2/|r_i - R_a| \\ & + \sum_n (p_n^2/2M)_n + \frac{1}{2} \sum_{a,b} Z_a Z_b e^2/|R_a - R_b| \end{aligned} \quad (5.1)$$

The origin of all electronic and nuclear coordinates is taken to be at the centre of the  $Gd^{3+}$  ion ( $n=0$ ). The first two terms are purely electronic operators, the third term is the interaction between the electrons and the nuclei, and the last two terms represent the nuclear kinetic energy and nucleus/nucleus interaction. Let us assume that the nuclei vibrate so that the deviations from their equilibrium positions are small. The third term in (5.1) then becomes

$$- \sum_n Z_n e^2 \left\{ 1/|\underline{r}_i - \underline{R}_{n0}| + \delta \underline{R}_n \cdot \nabla_n (1/|\underline{r}_i - \underline{R}_{n0}|) \right\} \quad (5.2)$$

where  $\underline{R}_{n0}$  is the equilibrium position of the  $n$ th nucleus, and it is to be understood that the second term is to be evaluated at this position. The first term in (5.2) is a purely electronic operator, and the second term contributes to the electron/phonon interactions. We therefore find that

$$H_{e1} = \sum_i (p_i^2/2m)_i - \sum_n Z_n e^2 / |\underline{r}_i - \underline{R}_{n0}| + \frac{1}{2} \sum_{i \neq j} e^2 / |\underline{r}_i - \underline{r}_j| \quad (5.3)$$

This of course is just the Hamiltonian (3.1) which was considered in the calculation of the inter-site mechanism for the static lattice. It will be convenient at this point to make the same approximations which were made in connection with (3.1). In particular we will assume that the core electrons associated with a given nucleus in the lattice may be absorbed into a new effective charge for that nucleus. Therefore for  $Gd^{3+}$ , the nuclear charge of +64 is combined with the 54 core electrons to give an effective nuclear charge of  $Z_n^* \approx 10$ . We will also make the assumption that in the second term in (5.3), we need only retain the interaction between the electrons and the  $Gd^{3+}$  nucleus. In chapter three it was argued that this was valid because the crystal field part of the second term in (5.3) was much smaller by comparison. The Hamiltonian (5.3) then becomes

$$H_{e1} = \sum_i (p_i^2/2m)_i - \sum_i Z_n^* e^2 / r_i + \frac{1}{2} \sum_{i \neq j} e^2 / |\underline{r}_i - \underline{r}_j| \quad (5.4)$$

It is not so easy to extract those parts of (5.1) which refer to lattice vibrations and interactions between the electrons and lattice vibrations. The reason is that the last term in (5.1) describes just the interaction between the bare nuclear charges. When the core-electrons are assumed to

be attached to the nuclei (which we have just done), the resulting 'ions' possess a definite structure, and as such the interaction between these ions is not well represented by a simple potential function [Pines 1963]. The same argument holds for the interaction between the electrons and these ions. Nevertheless, we will assume that it is possible to represent both of these interactions by using simple potential functions, for the sake of simplicity. We may then write

$$H_{ph} = \sum_{\mathbf{k}} (p^2/2M)_{\mathbf{k}} + \sum_{\mathbf{a}, \mathbf{b}} V(\mathbf{R}_{\mathbf{a}} - \mathbf{R}_{\mathbf{b}}) \quad (5.5)$$

$$H_{e/p} = - \sum_{\mathbf{a}} \mathbf{A} \mathbf{R}_{\mathbf{a}} \cdot \nabla V(\mathbf{r}_1 - \mathbf{R}_{\mathbf{a}}) \quad (5.6)$$

where in (5.6)  $V(\mathbf{r}_1 - \mathbf{R}_{\mathbf{a}})$  is a potential function representing the interaction of the valence electrons with the nuclei + core-electrons. Clearly (5.6) is a more general version of the second term in (5.2).

The effective operator to be used is that of equation (4.22):

$$H_{eff} = P_0^D H_d P_0^D = \sum_{\alpha=0} P_0^D H_d P_0^D P_0^D / (E_0 - E_0) \quad (5.7)$$

From now on we will drop the superscript 'D' from the projection operators  $P_0$ . In obtaining this expression for the effective operator in the dynamic lattice, we found that it was necessary to relegate all terms involving the lattice vibrations to the perturbation. It is now interesting to see how they appear in (5.7). From (4.9) we see that  $H_{ph}$  leads to terms of the form  $\alpha_{\mathbf{q}j}^\dagger \alpha_{\mathbf{q}j}$ , where  $\alpha_{\mathbf{q}j}$  and  $\alpha_{\mathbf{q}j}^\dagger$  are the phonon annihilators and creators. Such terms will appear in the first order correction in (5.8), and when a thermal average is performed, i.e.

$$\langle \alpha_{\mathbf{q}j}^\dagger \alpha_{\mathbf{q}j} \rangle \rightarrow \langle n_{\mathbf{q}j} \rangle \rightarrow [\exp(\hbar \omega(\mathbf{q}j)/kT) - 1]^{-1} \quad (5.8)$$

the result is a temperature dependent c-number, equal to the energy associated with a set of non-interacting phonons.  $H_{ph}$  does not contribute in the second (or higher) order corrections. The electron/phonon interaction cannot contribute to the first order correction in (5.7), because when the factor  $\mathbf{A} \mathbf{R}_{\mathbf{a}}$  in (5.6) is second quantised, it will lead to phonon operators

of the form  $\alpha_{qj}^* + \alpha_{qj}$  [Horton and Maradudin 1974]. When these operators are thermally averaged, the result is zero [Reissland 1972]. However,  $M_{\lambda/\rho}$  can appear in higher order corrections, and can then be expected to appear in the description of the various orbit-lattice interactions mentioned in chapter four.

### 5.3 Assumptions and Approximations

In order to make the calculation more tractable, it will be necessary to make some more simplifying assumptions and approximations, in addition to those which were made in the previous section. Most of these extra assumptions will be concerned with the lattice vibrations, because a paucity of experimental data means that an exact model will not be possible.

Let us first of all consider the electron/phonon interaction (5.6). In spite of the comments at the top of the previous page, one would expect that a good approximation to the potential  $V(\underline{r}_1 - \underline{R}_n)$  will be of the form

$$V(\underline{r}_1 - \underline{R}_n) = - \sum_i Z_n e^2 / |\underline{r}_1 - \underline{R}_n| \quad (5.9)$$

plus some small correction terms which allow for the actual structure of the core-electrons on the nuclei. (5.9) is very similar in form to the second term of (5.3), and it has already been argued that the crystal field component of this term is small enough to be neglected. When we take the gradient of (5.9), the result will contain terms which describe the change in the crystal field when the ligands start to vibrate. Provided that the displacements  $\delta \underline{R}_n$  are small enough, it would seem reasonable to assume that if the crystal field is small to start with, then the change in the crystal field when the ligands start to vibrate will be small too. We will therefore drop all terms in (5.6) for which  $n \neq 0$ . It then becomes

$$H_{\lambda/\rho} = \delta \underline{R}_0 \cdot \nabla V(\underline{r}_1) \quad (5.10)$$

where it is to be understood that (5.10) is equal to (5.6) evaluated only at  $n=0$ , with  $V$  given by (5.9).



The next approximations concern the model to be used for the lattice vibrations. It is obvious that the contribution from our mechanism to the effective SCCF operator (call it  $\mu_{\nu k}$  from now on) will be a function of the  $\delta R_0$ . To get  $\mu_{\nu k}$  as a function of temperature it will be necessary to perform some sort of averaging procedure which will require an explicit knowledge of the normal coordinates of the lattice. An exact calculation of the phonon spectrum of GdES is, to the very best of our knowledge, not available, and so some sort of approximation must be made. The usual approximation employed in this sort of calculation is the Debye/long wavelength approximation [Bates and Szymczak 1976], the principal advantage being that it is applicable to any crystal structure. We will consider this approximation in chapters six and seven, but for the majority of this thesis we will consider another approach. Since in these inter-site mechanisms we are concerned with excitations to oxygen atoms on those water molecules which are nearest neighbours of the  $Gd^{3+}$  ion (see fig. 3.1), it would seem that it is the motion of these nearest neighbours which we must model most accurately. Therefore we will consider a model in which we consider just the local modes of the  $Gd^{3+}$  ion, its nine water molecule neighbours, and those ethylsulphate radicals which are involved in the bonding to the water molecules. This model will be considered in detail in chapter seven. In this model we will also assume that the  $Gd^{3+}$  ion remains stationary in the lattice. Our main reason for wanting to do this is that it leads to a considerable reduction in the amount of algebra required to evaluate the matrix elements formed from the basis functions for the dynamic lattice. Given that we can only expect at best an order of magnitude estimate for the mechanism, this approximation should not be too severe. It also means that (5.10) is identically zero.

To summarise, the mechanism will be based on the following Hamiltonian:

$$H_d = \sum_i (p_i^2/2m)_i - \sum_i \sum_j \frac{e^2}{r_{ij}} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|r_i - r_j|} + H_{ph} \quad (5.11)$$

So we see that the Hamiltonian (5.1) has been reduced to essentially that for a static lattice. Therefore it would seem that we have removed all of the terms capable of contributing to our mechanism! This is not the case,

for the basis states for the dynamic lattice are different to those for the static lattice.

#### 5.4 Contributions to $\mu_{\text{eff}}$

To find the magnitude of  $\mu_{\text{eff}}$ , we need to know the combinations of second quantized operators which can appear in the second order correction (5.7), and which can give an BCCF-like operator when the angular momentum equivalences (2.16) are used. These combinations have already been given in chapter three, equations (3.7). We can carry over the same notation from this chapter, except that we must remember that the second quantized operators refer to electrons in the states (4.23), not the basis states for the static lattice. We also notice, from the final form of  $H_{\text{eff}}$  in (5.11), that the second quantized operators must arise from the same electronic operators as those for the static lattice, because  $H_{\text{eff}}$  cannot contribute to the second order effective operator. Because of the way that the unperturbed Hamiltonian for the dynamic lattice has been defined, retaining the concept of a family of states, it follows that the analysis from equations (3.7) to (3.21) is valid for the dynamic lattice too.

As a result of this, it is now straightforward to write down the magnitude  $\mu_{\text{eff}}$  of the effective BCCF operator generated by our inter-site mechanism, in the dynamic lattice. But first let us make some more specific definitions for the basis states in our system. Let  $|m\rangle$  represent a 4f-orbital on the  $\text{Gd}^{3+}$  ion (with magnetic quantum number  $m$ ) in the static lattice, and let  $|a\rangle$  be a 3s-orbital on a neighbouring oxygen. The corresponding orbitals in the dynamic lattice are given by

$$|m\rangle = \exp(-iS) |m\rangle \quad (5.12a)$$

$$|a\rangle = \exp(-iS) |a\rangle \quad (5.12b)$$

where the operator  $S$  is given by (4.24):

$$S = 1/(2\hbar) \sum_{\mathbf{R}} (P(\mathbf{R}_a) p_{\mathbf{R}a} + p_{\mathbf{R}a} P(\mathbf{R}_a)) \quad (5.13)$$

Now let us define a new type of orbital  $|W_n\rangle$ , which represents a localized Wannier function centred on the  $n^{\text{th}}$  member of the set of nine neighbouring oxygen atoms. The projection operator  $P(R_n)$  is then given by

$$P(R_n) = \sum_{W_n} |W_n\rangle \langle W_n| \quad (5.14)$$

where the sum will include two  $1s$ -functions, two  $2s$ -functions, four  $2p$ -functions and a  $3s$ -like function.

Bearing all of the considerations of this section in mind, we find that the contribution from the mechanism is given by

$$\mu_{\text{vh}} = \mu_1 + \mu_2 + \mu_3 + \mu_4 \quad (5.15)$$

where the various terms in (5.15) are given by

$$\begin{aligned} \mu_1 &= \lambda \sum_{\alpha} \langle m_1 | \exp(iB) X \exp(-iB) | \alpha \rangle \langle \alpha, m_2 | \exp(iX) U \exp(-iX) | m_3, m_1 \rangle \\ &\quad \times \langle m_1 | O_0^z | m_1 \rangle \\ \mu_2 &= \lambda \sum_{\alpha} \langle m_1 | \exp(iB) X \exp(-iB) | \alpha \rangle \langle \alpha, m_2 | \exp(iX) U \exp(-iX) | m_3, m_1 \rangle \\ &\quad \times \langle m_2 | O_0^z | m_3 \rangle \\ \mu_3 &= \lambda \sum_{\alpha} \langle m_1, m_2 | \exp(iX) U \exp(-iX) | \alpha, m_1 \rangle \langle \alpha, m_3 | \exp(iX) U \exp(-iX) | m_2, m_3 \rangle \\ &\quad \times \langle m_1 | O_0^z | m_1 \rangle \\ \mu_4 &= \lambda \sum_{\alpha} \langle m_1, m_2 | \exp(iX) U \exp(-iX) | \alpha, m_1 \rangle \langle \alpha, m_3 | \exp(iX) U \exp(-iX) | m_2, m_3 \rangle \\ &\quad \times \langle m_2 | O_0^z | m_2 \rangle \end{aligned} \quad (5.16)$$

In these expressions we have put  $X = S_1 + S_2$ , and  $\lambda = (-160/\Delta N \Delta N_2)$ . The operators  $X$  and  $U$  are given in equations (3.10) and (3.11). The subscripts in the expression for  $X$  indicate the coordinates of the electron for which (5.13) is defined.

The statement of the problem is now complete; our mechanism is to be obtained by evaluating and then adding together the expressions (5.16). The

next problem which we must consider is the evaluation of the matrix elements which appear in (5.16).

### 5.5 Evaluation of Matrix Elements

In order to evaluate the matrix elements which appear in (5.16), it is necessary to expand the exponentials which appear from the transformations (5.12a) and (5.12b). For the one-body terms we get

$$\begin{aligned} \exp(iS)\exp(-iS) &= X - i(XS - SX) + SXS \\ &- \frac{1}{2}(XS^2 + S^2X) \end{aligned} \quad (5.17)$$

and for the two-body terms we get

$$\begin{aligned} \exp(iS)U\exp(-iS) &= U - i(US_1 - S_1U) - i(US_2 - S_2U) \\ &+ S_1US_1 + S_2US_2 + S_1US_2 + S_2US_1 \\ &- \frac{1}{2}(S_1^2U + S_2^2U + US_1^2 + US_2^2) \\ &- S_1S_2U - US_1S_2 \end{aligned} \quad (5.18)$$

In (5.17) and (5.18), the exponentials have been expanded only to second order in  $S$ , because we wish to restrict ourselves to the harmonic approximation for the lattice vibrations. Given that  $S$  is defined by (5.13), with similar expressions for  $S_1$  and  $S_2$ , it is clear that the contributions (5.16) are going to become quite lengthy. Let us now examine what happens when one evaluates the matrix elements of the terms in (5.17) and (5.18).

From (5.17), consider the term  $iXS$ . The one-body matrix element of this term is

$$\begin{aligned} i\langle m_1 | XS | \alpha \rangle &= \frac{1}{2} \sum_{\alpha} \langle m_1 | X (P(R_{\alpha}) \nabla \cdot \vec{R}_{\alpha} + \nabla \cdot \vec{R}_{\alpha} P(R_{\alpha})) | \alpha \rangle \\ &= \frac{1}{2} \sum_{\alpha} \sum_{\beta} \langle m_1 | X | W_{\alpha} \rangle \langle W_{\beta} | \nabla \cdot \vec{R}_{\alpha} | \alpha \rangle \\ &+ \frac{1}{2} \langle m_1 | X \nabla \cdot \vec{R}_{\alpha} | \alpha \rangle \end{aligned} \quad (5.19)$$

To get this expression we have used (5.14), together with the fact that if the projection operator  $P(\underline{R}_a)$  acts on a wavefunction  $\Psi$ , the result is only non-zero if  $\Psi$  is centred on  $\underline{R}_a$  (remember that all basis functions are assumed to be mutually orthonormal).

From (5.18) consider the term  $S_1 U S_2$ . The matrix element  $\langle \alpha, m_3 | S_1 U S_2 | m_3, m_1 \rangle$  will contain (amongst others) a term of the form

$$- \frac{1}{2} \sum_{\alpha} \langle \alpha, m_3 | \underline{\nabla}_1 \cdot \underline{\delta R}_a P_1(\underline{R}_a) U P_2(\underline{R}_a) \underline{\nabla}_2 | m_3, m_1 \rangle$$

which with the help of (5.14) simplifies down to

$$- \frac{1}{2} \sum_{\alpha} \sum_{\underline{R}_a} \langle \alpha | \underline{\nabla}_1 \cdot \underline{\delta R}_a | W_a \rangle \langle W_a, m_3 | U | m_3, W_a \rangle \langle W_a | \underline{\nabla}_2 | m_3, m_1 \rangle \quad (5.20)$$

It will now be more convenient to expand the scalar products of the gradient operator with the ligand displacements  $\underline{\delta R}_a$ . That is, we will write

$$\underline{\nabla} \cdot \underline{\delta R}_a = \sum_{\mu} \nabla_{\mu} \delta R(n\mu)$$

where  $\mu$  represents the Cartesian coordinates  $x, y$  and  $z$ .  $\delta R(n\mu)$  is then the displacement of the  $n^{\text{th}}$  oxygen molecule in the  $\mu^{\text{th}}$  Cartesian direction.

On applying the above procedure to all of the terms in (5.17), we find that the one-body matrix element which appears in  $\mu_1$  and  $\mu_2$  is given by

$$\begin{aligned} & \langle m_1 | \exp(i\underline{\delta}) \exp(-i\underline{\delta}) | \alpha \rangle \\ &= A(\epsilon_1) - \sum_{\mu} \frac{1}{2} A(\epsilon_1, \alpha\mu) \delta R(\alpha\mu) + \sum_{\alpha\mu} \frac{1}{2} A(\epsilon_1, \mu\mu) \delta R(n\mu) \\ &+ \sum_{\mu_1\mu_2} \left( A(\epsilon_1, \mu_1\alpha\nu) \delta R(\mu_1) \delta R(b\nu) + A(\epsilon_1, \mu_1\mu_2\nu) \delta R(\mu_1) \delta R(m\nu) \right) \\ &+ \sum_{\alpha\mu} \sum_{\alpha\nu} A(\epsilon_1, \mu_1\mu_2\nu) \delta R(n\mu) \delta R(m\nu) \end{aligned} \quad (5.21)$$

where the various constants in (5.21) are given by

$$\begin{aligned}
A(e_1) &= \langle m_1 | X | \alpha \rangle \\
A(e_1, \alpha\mu) &= \langle m_1 | X \nabla_\mu | \alpha \rangle \\
A(e_1, n\mu) &= \sum_{m_2} ( \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | X | \alpha \rangle - \langle W_n | \nabla_\mu | \alpha \rangle \langle m_1 | X | W_n \rangle ) \\
A(e_1, n\mu\alpha\nu) &= \eta \sum_{m_2} ( \langle m_1 | X | W_n \rangle \langle W_n | \nabla_\mu \nabla_\nu | \alpha \rangle - 2 \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | X \nabla_\nu | \alpha \rangle \\
&\quad + \langle m_1 | X \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | \alpha \rangle ) \\
A(e_1, n\mu\nu\nu) &= \eta \sum_{m_2} ( \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu X | \alpha \rangle + \langle m_1 | X \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | \alpha \rangle ) \\
A(e_1, n\mu\nu\nu) &= \eta \sum_{m_2} ( \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | W_m \rangle \langle W_m | X | \alpha \rangle \\
&\quad - 2 \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | X | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle \\
&\quad + \langle m_1 | X | W_n \rangle \langle W_n | \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle ) \quad (5.22)
\end{aligned}$$

We have used the symbol  $e_1$  in the coefficients in (5.22) to indicate that these terms originate from the one-body matrix element.

The two-body matrix element of  $\mu_1$  and  $\mu_2$  is given by

$$\begin{aligned}
&\langle \alpha, m_2 | \exp(i\beta_1 + i\beta_2) U \exp(-i\beta_1 - i\beta_2) | m_3, m_1 \rangle \\
&= B(e_2) + \sum_{\mu} \eta B(e_2, \alpha\mu) \delta R(\alpha\mu) + \sum_{\mu} \eta B(e_2, n\mu) \delta R(n\mu) \\
&+ \sum_{\mu\nu} ( B(e_2, \alpha\mu\nu) \delta R(n\mu) \delta R(b\nu) + B(e_2, n\mu\nu) \delta R(n\mu) \delta R(m\nu) ) \\
&+ \sum_{\mu\nu} B(e_2, n\mu\nu) \delta R(n\mu) \delta R(m\nu) \quad (5.23)
\end{aligned}$$

The various constants in (5.23) are given by

$$\begin{aligned}
B(e_2) &= \langle \alpha, m_2 | U | m_3, m_1 \rangle \\
B(e_2, \alpha\mu) &= \langle \alpha, m_2 | \nabla_\mu U | m_3, m_1 \rangle \\
B(e_2, n\mu) &= \sum_{m_2} ( \langle \alpha | \nabla_\mu | W_n \rangle \langle W_n, m_2 | U | m_3, m_1 \rangle \\
&\quad + \langle m_2 | \nabla_\mu | W_n \rangle \langle \alpha, W_n | U | m_3, m_1 \rangle \\
&\quad - \langle W_n | \nabla_\mu | m_2 \rangle \langle \alpha, m_2 | U | W_n, m_1 \rangle )
\end{aligned}$$

$$- \langle W_a | \nabla_\mu | m_1 \rangle \langle \alpha, m_3 | U | m_3, W_a \rangle )$$

$$\begin{aligned} B(\alpha_2, \alpha\mu\nu) = & \hbar \sum_{W_a} ( \langle W_a, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle \alpha | \nabla_\mu | W_a \rangle \\ & + \langle W_a, m_3 | U | m_3, m_1 \rangle \langle \alpha | \nabla_\mu \nabla | W_a \rangle \\ & - 2 \langle \alpha, m_3 | \nabla_{1\mu} U | W_a, m_1 \rangle \langle W_a | \nabla_\nu | m_3 \rangle \\ & - 2 \langle \alpha, m_3 | \nabla_{1\mu} U | m_3, W_a \rangle \langle W_a | \nabla_\nu | m_1 \rangle \\ & + 2 \langle \alpha, W_a | \nabla_{1\mu} U | m_3, m_1 \rangle \langle m_3 | \nabla_\nu | W_a \rangle ) \end{aligned} \quad (5.24)$$

$$\begin{aligned} B(\alpha_2, \alpha\mu\nu) = & \hbar \sum_{W_a} ( \langle W_a, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle \alpha | \nabla_\mu | W_a \rangle \\ & + \langle \alpha, W_a | \nabla_{2\nu} U | m_3, m_1 \rangle \langle m_3 | \nabla_\mu | W_a \rangle \\ & + \langle \alpha, m_3 | U \nabla_{1\mu} | W_a, m_1 \rangle \langle W_a | \nabla_\nu | m_3 \rangle \\ & + \langle \alpha, m_3 | U \nabla_{2\mu} | m_3, W_a \rangle \langle W_a | \nabla_\nu | m_1 \rangle ) \end{aligned}$$

$$\begin{aligned} B(\alpha_2, \alpha\mu\nu) = & \hbar \sum_{W_a} \sum_{W_b} ( \langle \alpha | \nabla_\mu | W_a \rangle \langle W_a | \nabla_\nu | W_b \rangle \langle W_b, m_3 | U | m_3, m_1 \rangle \\ & + \langle m_3 | \nabla_\mu | W_a \rangle \langle W_a | \nabla_\nu | W_b \rangle \langle \alpha, W_b | U | m_3, m_1 \rangle \\ & + \langle W_a | \nabla_\mu | W_b \rangle \langle W_b | \nabla_\nu | m_3 \rangle \langle \alpha, m_3 | U | W_a, m_1 \rangle \\ & + \langle W_a | \nabla_\mu | W_b \rangle \langle W_b | \nabla_\nu | m_1 \rangle \langle \alpha, m_3 | U | m_3, W_a \rangle \\ & - 2 \langle \alpha | \nabla_\mu | W_a \rangle \langle W_b | \nabla_\nu | m_1 \rangle \langle W_a, m_3 | U | m_3, W_b \rangle \\ & - 2 \langle m_3 | \nabla_\mu | W_a \rangle \langle W_b | \nabla_\nu | m_3 \rangle \langle \alpha, W_a | U | W_b, m_1 \rangle \\ & - 2 \langle \alpha | \nabla_\mu | W_a \rangle \langle W_b | \nabla_\nu | m_3 \rangle \langle W_a, m_3 | U | W_b, m_1 \rangle \\ & - 2 \langle m_3 | \nabla_\mu | W_a \rangle \langle W_b | \nabla_\nu | m_1 \rangle \langle \alpha, W_a | U | m_3, W_b \rangle \\ & + 2 \langle W_a | \nabla_\mu | m_1 \rangle \langle W_b | \nabla_\nu | m_3 \rangle \langle \alpha, m_3 | U | W_a, W_b \rangle \\ & + 2 \langle \alpha | \nabla_\mu | W_a \rangle \langle m_3 | \nabla_\nu | W_b \rangle \langle W_a, W_b | U | m_3, m_1 \rangle ) \end{aligned}$$

In these expressions, a subscript 1 or 2 is added to the gradients which appear in the two-body matrix elements, to indicate which set of coordinates the gradient acts upon. The symbol  $s_2$  is used to indicate that these terms originate from the matrix element in (5.23).

The matrix element

$$\langle \alpha, m_g | \exp(iS_1 + iS_2) U \exp(-iS_1 - iS_2) | m_a, m_g \rangle$$

can be evaluated in the same way as the previous one. It takes precisely the same form as (5.23), except that the coefficients which appear before the ligand displacements are different. We may use the same notation for the coefficients of this matrix element, except that we will use the symbol  $e_3$  instead of  $e_2$  to indicate the matrix element for which the new coefficients are defined. For instance the term which appears with no ionic displacements is  $B(e_3)$ . We find that

$$\begin{aligned} B(e_3) &= \langle \alpha, m_g | U | m_a, m_g \rangle \\ B(e_3, \alpha\mu) &= \langle \alpha, m_g | \nabla_\mu U | m_a, m_g \rangle \\ B(e_3, \alpha\mu) &= \sum_{W_a} ( \langle \alpha | \nabla_\mu | W_a \rangle \langle W_a, m_g | U | m_a, m_g \rangle \\ &\quad + \langle m_g | \nabla_\mu | W_a \rangle \langle \alpha, m_g | U | W_a, m_g \rangle \\ &\quad - \langle W_a | \nabla_\mu | m_a \rangle \langle \alpha, m_g | U | W_a, m_g \rangle \\ &\quad - \langle W_a | \nabla_\mu | m_g \rangle \langle \alpha, m_g | U | m_a, W_a \rangle ) \\ B(e_3, \alpha\mu\nu) &= h \sum_{W_a} ( \langle W_a, m_g | \nabla_\mu U | m_a, m_g \rangle \langle \alpha | \nabla_\nu | W_a \rangle \\ &\quad + \langle W_a, m_g | U | m_a, m_g \rangle \langle \alpha | \nabla_\mu \nabla_\nu | W_a \rangle \\ &\quad - 2 \langle \alpha, m_g | \nabla_\mu U | W_a, m_g \rangle \langle W_a | \nabla_\nu | m_a \rangle \\ &\quad - 2 \langle \alpha, m_g | \nabla_\mu U | m_a, W_a \rangle \langle W_a | \nabla_\nu | m_g \rangle \\ &\quad + 2 \langle \alpha, W_a | \nabla_\mu U | m_a, m_g \rangle \langle m_g | \nabla_\nu | W_a \rangle ) \\ B(e_3, \alpha\mu\nu) &= h \sum_{W_a} ( \langle W_a, m_g | \nabla_\mu U | m_a, m_g \rangle \langle \alpha | \nabla_\nu | W_a \rangle \\ &\quad + \langle \alpha, W_a | \nabla_\mu U | m_a, m_g \rangle \langle m_g | \nabla_\nu | W_a \rangle \\ &\quad + \langle \alpha, m_g | U \nabla_\mu | W_a, m_g \rangle \langle W_a | \nabla_\nu | m_a \rangle \\ &\quad + \langle \alpha, m_g | U \nabla_\mu | m_a, W_a \rangle \langle W_a | \nabla_\nu | m_g \rangle ) \\ B(e_3, \alpha\mu\nu) &= h \sum_{W_a} \sum_{W_b} ( \langle \alpha | \nabla_\mu | W_a \rangle \langle W_a | \nabla_\nu | W_b \rangle \langle W_b, m_g | U | m_a, m_g \rangle \end{aligned} \quad (5.25)$$



$$\begin{aligned}
& + \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | W_n \rangle \langle \alpha, W_n | U | m_2, m_2 \rangle \\
& + \langle W_n | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle \alpha, m_2 | U | W_n, m_2 \rangle \\
& + \langle W_n | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle \alpha, m_2 | U | m_2, W_n \rangle \\
& - 2 \langle \alpha | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle W_n, m_2 | U | m_2, W_n \rangle \\
& - 2 \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle \alpha, W_n | U | W_n, m_2 \rangle \\
& - 2 \langle \alpha | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle W_n, m_2 | U | W_n, m_2 \rangle \\
& - 2 \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle \alpha, W_n | U | m_2, W_n \rangle \\
& + 2 \langle W_n | \nabla_\mu | m_2 \rangle \langle W_n | \nabla_\nu | m_2 \rangle \langle \alpha, m_2 | U | W_n, W_n \rangle \\
& + 2 \langle \alpha | \nabla_\mu | W_n \rangle \langle m_2 | \nabla_\nu | W_n \rangle \langle W_n, W_n | U | m_2, m_2 \rangle
\end{aligned}$$

The other two-body matrix element in (5.16),

$$\langle m_1, m_2 | \exp(i\beta_1 + i\beta_2) U \exp(-i\beta_1 - i\beta_2) | \alpha, m_1 \rangle$$

also takes the form (5.23). The coefficients which multiply the ligand displacements will be labelled by the symbol  $\epsilon_4$ . They are given by

$$\begin{aligned}
B(\epsilon_4) &= \langle m_1, m_2 | U | \alpha, m_1 \rangle \\
B(\epsilon_4, \alpha_\mu) &= \langle m_1, m_2 | U \nabla_\mu | \alpha, m_1 \rangle \\
B(\epsilon_4, n_\mu) &= \sum_{m_2} ( \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n, m_2 | U | \alpha, m_1 \rangle \\
&\quad + \langle m_2 | \nabla_\mu | W_n \rangle \langle m_1, W_n | U | \alpha, m_1 \rangle \\
&\quad - \langle W_n | \nabla_\mu | \alpha \rangle \langle m_1, m_2 | U | W_n, m_1 \rangle \\
&\quad - \langle W_n | \nabla_\mu | m_1 \rangle \langle m_1, m_2 | U | \alpha, W_n \rangle ) \\
B(\epsilon_4, \alpha_\mu \nu) &= \frac{1}{2} \sum_{m_2} ( \langle m_1, m_2 | U | W_n, m_1 \rangle \langle W_n | \nabla_\nu \nabla_\mu | \alpha \rangle \\
&\quad + \langle m_1, m_2 | U \nabla_\nu | W_n, m_1 \rangle \langle W_n | \nabla_\mu | \alpha \rangle \\
&\quad - 2 \langle m_1, W_n | U \nabla_\nu | \alpha, m_1 \rangle \langle m_2 | \nabla_\mu | W_n \rangle \\
&\quad - 2 \langle W_n, m_2 | U \nabla_\nu | \alpha, m_1 \rangle \langle m_1 | \nabla_\mu | W_n \rangle )
\end{aligned}$$

$$+ 2 \langle m_1, m_2 | U \nabla_{1\mu} | \alpha, W_n \rangle \langle W_n | \nabla_\nu | W_m \rangle \quad (5.26)$$

$$\begin{aligned} B(\alpha\alpha, m_1 m_2) &= \hbar \sum_{W_n} \left( \langle W_n, m_2 | \nabla_{1\nu} U | \alpha, m_1 \rangle \langle m_1 | \nabla_\mu | W_n \rangle \right. \\ &\quad + \langle m_1, W_n | \nabla_{2\nu} U | \alpha, m_1 \rangle \langle m_2 | \nabla_\mu | W_n \rangle \\ &\quad + \langle m_1, m_2 | U \nabla_{1\mu} | W_n, m_1 \rangle \langle W_n | \nabla_\nu | \alpha \rangle \\ &\quad \left. + \langle m_1, m_2 | U \nabla_{2\mu} | \alpha, W_n \rangle \langle W_n | \nabla_\nu | m_1 \rangle \right) \\ B(\alpha\alpha, n_1 m_2) &= \hbar \sum_{W_n} \sum_{W_m} \left( \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | W_m \rangle \langle W_m, m_2 | U | \alpha, m_1 \rangle \right. \\ &\quad + \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | W_m \rangle \langle m_1, W_m | U | \alpha, m_1 \rangle \\ &\quad + \langle W_n | \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle \langle m_1, m_2 | U | W_n, m_1 \rangle \\ &\quad + \langle W_n | \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | m_1 \rangle \langle m_1, m_2 | U | \alpha, W_n \rangle \\ &\quad - 2 \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_1 \rangle \langle W_m, m_2 | U | \alpha, W_m \rangle \\ &\quad - 2 \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | \alpha \rangle \langle m_1, W_n | U | W_m, m_1 \rangle \\ &\quad - 2 \langle m_1 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | \alpha \rangle \langle W_m, m_2 | U | W_n, m_1 \rangle \\ &\quad - 2 \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_1 \rangle \langle m_1, W_n | U | \alpha, W_m \rangle \\ &\quad + 2 \langle W_n | \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle \langle m_1, m_2 | U | W_n, W_m \rangle \\ &\quad \left. + 2 \langle m_1 | \nabla_\mu | W_m \rangle \langle m_2 | \nabla_\nu | W_m \rangle \langle W_m, W_m | U | \alpha, m_1 \rangle \right) \end{aligned}$$

We have now obtained expressions for all of the matrix elements which appear in the contributions (5.16), in terms of matrix elements involving basis functions for the static lattice. We can now substitute back into (5.16), and obtain an expression for  $\mu_{\nu\lambda}$ .

#### 5.6 Contributions in the Harmonic Approximation

Before we substitute the expressions (5.21) to (5.26) back into (5.16), there are a few points we should note. Firstly, since we are restricting ourselves to the harmonic approximation for the lattice vibrations, we can neglect all terms whose dependence on the ligand displacements is higher than quadratic. Secondly, terms linear in the ligand displacements may also be dropped because  $\langle \delta R \rangle = 0$ . Thirdly, each contribution in (5.16)

will contain a term which contains no ligand displacements. These terms simply correspond to the mechanism of chapter three, and so they can be ignored too. Bearing these three considerations in mind, we find that

$$\begin{aligned}
 \mu_1 + \mu_2 = & \lambda \sum_r i \sum_{\alpha\beta} A_r(\alpha\alpha\mu\nu) \delta R(\alpha\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} A_r(\alpha\alpha\mu\nu) \delta R(\alpha\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} A_r(\alpha\mu\mu\nu) \delta R(\mu\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} A_r(\alpha\mu\mu\nu) \delta R(\mu\mu) \delta R(\alpha\nu) \quad (5.27) \\
 & \times ( \langle m_1 | O_2^0 | m_1 \rangle + \langle m_3 | O_2^0 | m_3 \rangle )
 \end{aligned}$$

where the various terms in (5.27) are given by

$$\begin{aligned}
 A_r(\alpha\alpha\mu\nu) &= -\frac{1}{2} A(\epsilon_1, \alpha\mu) \cdot B(\epsilon_2, \alpha\nu) \\
 A_r(\alpha\mu\mu\nu) &= A(\epsilon_1, \alpha\mu\nu) \cdot B(\epsilon_2) + \frac{1}{2} A(\epsilon_1, \mu\nu) \cdot B(\epsilon_2, \alpha\mu) \\
 &\quad + B(\epsilon_2, \alpha\mu\nu) \cdot A(\epsilon_1) - \frac{1}{2} A(\epsilon_1, \alpha\mu) \cdot B(\epsilon_2, \mu\nu) \quad (5.28) \\
 A_r(\alpha\mu\mu\nu) &= B(\epsilon_2) \cdot A(\epsilon_1, \mu\mu\nu) + A(\epsilon_1) \cdot B(\epsilon_2, \mu\mu\nu) \\
 A_r(\alpha\mu\mu\nu) &= B(\epsilon_2) \cdot A(\epsilon_1, \mu\mu\nu) + \frac{1}{2} A(\epsilon_1, \mu\nu) \cdot B(\epsilon_2, \mu\mu) \\
 &\quad + A(\epsilon_1) \cdot B(\epsilon_2, \mu\mu\nu)
 \end{aligned}$$

In these terms the subscript 'r' has the same meaning as in chapter three; that is, it is shorthand for the set of variables  $\{m_1, m_3, \alpha\}$ . It is used here as a reminder that the terms in (5.27) and (5.28) are also functions of the 4f-quantum numbers  $m_1$  and  $m_3$ , and the oxygen orbital  $\alpha$ .

Similarly we find that the other two contributions of (5.16) are given by

$$\begin{aligned}
 \mu_3 + \mu_4 = & \lambda \sum_i i \sum_{\mu\nu} C_i(\alpha\alpha\mu\nu) \delta R(\alpha\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} C_i(\alpha\alpha\mu\nu) \delta R(\alpha\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} C_i(\alpha\mu\mu\nu) \delta R(\mu\mu) \delta R(\alpha\nu) \\
 & + \sum_{\alpha\beta\nu} C_i(\alpha\mu\mu\nu) \delta R(\mu\mu) \delta R(\alpha\nu) \quad (5.29)
 \end{aligned}$$

$$x \left( \langle m_1 | O_0 | m_1 \rangle + \langle m_2 | O_0 | m_2 \rangle \right)$$

The various terms in (5.29) are given by

$$\begin{aligned} C_1(\alpha\alpha\mu\nu) &= -\frac{1}{2} B(\epsilon_3, \alpha\mu) \cdot B(\epsilon_4, \alpha\nu) \\ C_1(\alpha\mu\nu) &= B(\epsilon_4, \alpha\mu\nu) \cdot B(\epsilon_3) + \frac{1}{2} B(\epsilon_3, \mu\nu) \cdot B(\epsilon_4, \alpha\mu) \\ &\quad + B(\epsilon_3, \alpha\mu\nu) \cdot B(\epsilon_4) - \frac{1}{2} B(\epsilon_4, \alpha\mu) \cdot B(\epsilon_3, \mu\nu) \quad (5.30) \\ C_1(\mu\mu\nu) &= B(\epsilon_4) \cdot B(\epsilon_3, \mu\mu\nu) + B(\epsilon_3) \cdot B(\epsilon_4, \mu\mu\nu) \\ C_1(\mu\nu\mu) &= B(\epsilon_3) \cdot B(\epsilon_4, \mu\nu\mu) + \frac{1}{2} A(\epsilon_4, \mu\nu) \cdot B(\epsilon_3, \mu\mu) \\ &\quad + B(\epsilon_4) \cdot B(\epsilon_3, \mu\nu\mu) \end{aligned}$$

The subscript 't' is used in (5.29) and (5.30) for the same reason that  $r$  is used in (5.27) and (5.28), and is shorthand for the set of variables  $(m_1, m_2, m_3, \alpha)$ . We have now succeeded in expressing our mechanism in terms of the ligand displacements. The magnitude of  $\mu_{bb}$  is to be found by evaluating (5.27) and (5.29).

## 5.7 Summary and Discussion

In this chapter we have concentrated on the formulation of the problem to be solved. This has resulted in expressions (5.27) to (5.30). We have made several approximations in getting to these expressions. In particular, we have chosen to assume that the  $Gd^{3+}$  ion remains stationary in the lattice. This results in (5.27) and (5.29) being much simpler than they otherwise would have been. If this assumption had not been made, then (5.27) and (5.29) would contain three extra terms, associated with ligand products

$$\delta R(\mu\mu)\delta R(\alpha\nu), \delta R(\mu\mu)\delta R(\alpha\nu), \delta R(\mu\mu)\delta R(\mu\nu)$$

where 'a' is used to label a displacement of the  $Gd^{3+}$  ion. The assumption therefore results in almost a halving of the algebraic complexity of the problem. The assumption also results in the electron/phonon interactions becoming identically zero.

The formalism of this chapter also demonstrates the value of the simple approach which we took to the formulation of the Method of Stevens in the dynamic lattice. The retention of the concept of states being split up into distinct families, and the simple form of the projection operators for the dynamic lattice both mean that an expression for  $\mu_{\nu\lambda}$  could be obtained using a procedure analogous to that given in chapter three. The intrinsic simplicity of this approach would almost certainly be lost if one of the alternative schemes outlined in chapter four had been used.

In the next chapter we will consider the problem of rewriting the ligand products in a form which is more convenient for obtaining the temperature dependence of  $\mu_{\nu\lambda}$ . That is, we will introduce the normal coordinates of the lattice.

## CHAPTER 6

### Temperature Dependence of $\mu_{\text{L}}$

#### 6.1 Introduction

In the previous chapter we obtained an expression for  $\mu_{\text{L}}$  in terms of the displacements of the neighbouring oxygen atoms and matrix elements involving basis functions defined for the static lattice. The problem of obtaining numerical estimates of  $\mu_{\text{L}}$  is therefore split up into two stages: 1) the evaluation of the electronic matrix elements, and 2) the conversion of the products of displacements into temperature dependant factors. In this chapter we will concentrate on the second stage of the problem.

The conversion of products of ligand displacements into temperature dependent factors basically involves the calculation of quantities such as  $\langle \delta R(a) \delta R(b) \rangle$ , where  $a$  and  $b$  are labels for any two of the nine surrounding oxygen atoms, and the brackets  $\langle \dots \rangle$  denote a thermal average. Such a calculation is made easier if the displacements  $\delta R$  are written in terms of the normal coordinates of the lattice. In doing this we will focus most of our attention on a model in which we consider just the normal coordinates of the nine oxygen atoms surrounding the  $\text{Gd}^{3+}$  ion (we will refer to this as the 'Restricted' model of lattice vibrations), but we will also consider what happens in the more general case where we include all of the vibrational modes of the crystal.

In the next section we will derive a general expression for  $\langle \delta R(a) \delta R(b) \rangle$  in terms of the temperature of the lattice, and in section 6.3 we will consider how to specialise it for the Restricted model of lattice vibrations mentioned above. This is done most easily by considering the special case of a crystal composed of just a single unit cell. Section 6.4 will be concerned with some of the ways in which we can incorporate all of the normal coordinates of the lattice. The results of this section will be of the greatest importance in the next chapter. Finally in section 6.5 we will collect together the results of equations (5.27) and (5.29), and the

results of section 6.3, and we will present an expression for  $\mu_{ab}$  as a function of the temperature of the lattice.

## 6.2 The General Problem

In order to obtain the thermal average  $\langle \delta R(a\mu) \delta R(b\nu) \rangle$ , it is best to start by rewriting the displacements in terms of the normal coordinates of the lattice. Let us assume that the lattice is composed of  $N$  unit cells, with  $r$  basis atoms per unit cell. It can be shown that the displacement  $\delta R(a\mu)$  may be written in the following way (Maradudin et al. 1971):

$$\delta R(a\mu) = (NM_a)^{-1/2} \sum_{gj} a_{\mu}(a|gj) Q(gj) \exp[ig \cdot X(l)] \quad (6.1)$$

In this expression,  $M_a$  is the mass of the  $a^{\text{th}}$  oxygen atom, and  $X(l)$  is a vector from a convenient origin to a suitable reference point in the unit cell containing the oxygen atom (the  $l^{\text{th}}$ ). The  $Q(gj)$  are the normal coordinates of the lattice, and they are labelled with a wavevector  $g$  and a branch  $j$ . The importance of the normal coordinates stems from the fact that the vibrational Hamiltonian for the lattice takes the following form when written in terms of them, in the harmonic approximation:

$$H_{ph} = \frac{1}{2} \sum_{gj} [\dot{Q}(gj)^2 + \omega(gj)^2 Q(gj)^2] \quad (6.2)$$

That is,  $H_{ph}$  becomes diagonal. Note that  $H_{ph}$  is essentially the same as  $H_{ph}$ , given in (5.5), with the inter-ionic potential expanded to second order in a Taylor series about the equilibrium positions of the nuclei. The  $a_{\mu}(a|gj)$  are coefficients obtained from the procedure of diagonalising  $H_{ph}$ , and if (6.2) is to be valid they must satisfy the following orthonormality and closure relations (Maradudin et al. 1971):

$$\sum_{a\mu} a_{\mu}(a|gj) a_{\mu}(a|gj') = \delta_{jj'} \quad (6.3)$$

$$\sum_{gj} a_{\mu}(a|gj) a_{\nu}(b|gj) = \delta_{ab} \delta_{\mu\nu} \quad (6.4)$$

Strictly speaking, the symbols 'a' and 'b' in these expressions should not be restricted to the nine nearest neighbouring oxygen atoms. Instead they

should refer to all of the atoms in the unit cell. If we look again at figure 1.3, then we see that the unit cell contains ethylsulphate radicals, as well as the nine neighbouring water molecules and a  $Gd^{3+}$  ion. When we consider the Restricted model of the lattice vibrations, it will be convenient to ignore the motion of the ethylsulphate radicals. Since we have already assumed that the  $Gd^{3+}$  ion is stationary in the lattice, and if we make the further assumption that the hydrogen atoms belonging to the neighbouring water molecules move rigidly with the oxygen atoms, then it follows that (6.3) and (6.4) are correct as written, if we wish to consider all of the remaining modes of the lattice. However, these approximations will make little difference to the numerical results, because the models we are going to use (Debye and Einstein models) lead to results which are independent of the number of basis atoms in the unit cell (see equations (6.12) and (6.14)). From now on though, when we refer to the motion of an 'oxygen atom', it is to be understood that we are referring to the motion of one of the nine neighbouring water molecules, under the assumption that the hydrogen atoms move rigidly with the oxygen atom.

The normal coordinates can also be written in terms of phonon annihilators and creators. One finds that [Maradudin et al. 1971]:

$$Q(gj) = (\hbar/2M(\rho g))^{1/2} (\alpha_{gj}^{\dagger} + \alpha_{-gj}) \quad (6.5)$$

The meaning of the symbols  $g$  and  $j$  is clearer in (6.5), for they can now be related to the properties of the phonons created by  $\alpha_{gj}^{\dagger}$ . From (6.5) we can obtain the well known result

$$Q^*(gj) = Q(-gj) \quad (6.6)$$

We now have all of the information we require to find the thermal average  $\langle \delta R(a\mu) \delta R(b\nu) \rangle$ . From now on we will abbreviate this quantity by writing it as  $T(a\mu\nu)$ . If both displacements are written in the form (6.1), and we use (6.5) and (6.6), then we find that the average is given by

$$T(a\mu\nu) = \hbar/(2NM) \sum_{g,j} \omega(gj)^{-1} e^{i(g(a\mu - b\nu))} \langle (\alpha_{gj}^{\dagger})^2 \rangle \quad (6.7)$$



where we have put  $M_s = M_b = M$ , and  $n_{qj} = \alpha_{qj}^\dagger \alpha_{qj}$ . The last term in (6.7) involves the thermal average of the occupation number of the phonon mode with wavevector  $q$ , belonging to the  $j^{\text{th}}$  branch. This average is just the Bose-Einstein distribution for phonons [Maradudin et al., 1971]:

$$\langle n_{qj} \rangle = \langle \exp(\beta \hbar \omega(jq)) \rangle^{-1} \quad (6.8)$$

where we have put  $\beta = 1/k_B T$ . Substituting back into (6.7) gives

$$T(\text{abuv}) = \hbar / (2NM) \sum_{qj} \omega(jq)^{-1} e_v(biqj) e_u(alqj) \coth(\beta \hbar \omega(jq)) \quad (6.9)$$

This is the result we seek. The rest of the work of this chapter will follow directly from this result.

### 6.3 Thermal Averages in the Restricted Model

In the Restricted model of the lattice vibrations, we wish to consider only the motion of the nine oxygen atoms which surround the  $\text{Gd}^{3+}$  ion under consideration. The rest of the vibrational modes are ignored. The easiest way to specialise (6.9) to this case is to insist that  $N=1$ , i.e. we consider a crystal composed of just one unit cell. We will ignore the motion of the ethylsulphate radicals in the unit cell, so that we consider only the 27 normal coordinates of the oxygen atoms in the Restricted model.

There is an important consequence which arises from setting  $N=1$  in (6.9). For any branch of the phonon spectrum, there are exactly  $N$  allowed values of  $q$ . Therefore if  $N=1$ , there is effectively only one phonon mode per branch, and so the wavevector  $q$  can be dropped from (6.9). We therefore find that, in the Restricted model of lattice vibrations

$$T_s(\text{abuv}) = \hbar / (2M) \sum_j \omega(j)^{-1} \beta_j(bv) \beta_j(au) \coth(\beta \hbar \omega(j)) \quad (6.10)$$

where the  $\beta_j(au)$  are coefficients analogous to the coefficients  $e_u(alqj)$  in the more general case. It turns out that the  $\beta$  coefficients are much easier to calculate than the  $e$  coefficients, because there is only a finite number of them. In addition, they form a discrete set of quantities,

rather than a continuous set. In (6.10),  $j$  now labels the individual normal coordinates of the oxygen atoms.

One might ask at this stage how it is that we can apply these statistical ideas to a system consisting of only nine vibrating atoms, for it would seem that statistical fluctuations ( $\propto 1/\sqrt{N}$ , where  $N$  = number of particles in the system) would make the concept of a thermal average meaningless. The answer of course is that we cannot apply them if the system is an isolated one, but the system is not isolated; it is part of a crystal lattice which consists of many unit cells coupled together. We may therefore consider a single unit cell as being coupled to a heat bath which consists of all of the other unit cells in the crystal. Provided that the coupling is weak and that there are a large number of unit cells, it is possible to consider any one unit cell as being in thermal equilibrium (Feynmann 1972; Mandl 1967). We will assume that both criteria hold. The assumption about the unit cell being coupled weakly to the rest of the lattice is probably a reasonably good one, because the coupling arises from hydrogen bonds between the water molecules and the ethylsulphate radicals. We will say more about this in the next chapter. Provided that the crystal has macroscopic dimensions, the number of unit cells will be large.

#### 6.4. Models of the Whole Lattice.

The evaluation of (6.9) is in general a fairly difficult problem, because one needs to have an explicit knowledge of the normal coordinates, and also a knowledge of the phonon spectrum  $\omega(j)$  (Maradudin et al. p308). A knowledge of the normal coordinates is required because of the appearance of the  $a$  coefficients in (6.9). This problem can be circumvented, and an approximation to the thermal average can be obtained, by putting  $a = b$ ,  $\mu = \nu$  in (6.9) and then summing over  $a$  and  $\mu$ . With the help of (6.3) this gives

$$\sum_{a\mu} \langle R(a\mu) R(a\mu) \rangle = \hbar / (2N\hbar) \sum_j \omega(j)^{-1} \coth(\frac{1}{2}\hbar\omega(j)) \quad (6.11)$$

To the best of our knowledge, the exact form of the phonon spectrum  $\omega(j)$  for GdES is not available, and so we must use some sort of approximation. The most common of these are the Debye and Einstein models (Ziman 1963).

In the Einstein model, the vibrational motion of any one atom is assumed to be independent of the motion of the other atoms.  $\omega(jg)$  is then assumed to be a constant, independent of  $j$  and  $g$ . If we make this approximation in (6.11), and make the further assumption that  $\langle \delta R(\mu) \delta R(\mu) \rangle$  is independent of  $a$  and  $\mu$  (i.e. that the crystal is isotropic), we find that

$$\langle \delta R(\mu) \delta R(\mu) \rangle = \hbar / (2M\omega_E) \coth(\hbar\beta\hbar\omega_E) \quad (6.12)$$

$\omega_E$  is called the Einstein frequency, and is equal to the constant frequency assumed for the atomic vibrations. It is often chosen so that theory matches up with the relevant experimental data.

The Einstein approximation is a reasonable approximation for the optical phonon branches, because the dispersion curve  $\omega(jg) \sim q$  is often very flat for these branches. However it cannot be considered a good approximation for the acoustic branches, because  $\omega(jg) \rightarrow 0$  as  $q \rightarrow 0$  for the acoustic modes. A better approximation for the acoustic branches is the Debye approximation, in which the vibrational modes of the crystal are replaced by the vibrational modes of an elastic continuum. The dispersion curve now becomes linear, so that  $\omega(jg) = q$ . It is also convenient to introduce a density of states function  $D(\omega)d\omega$ , equal to the number of vibrational modes with frequencies between  $\omega$  and  $\omega + d\omega$ . The sum over  $j$  and  $g$  in (6.11) can then be replaced by an integration over  $\omega$ , with a fixed upper limit chosen so that the correct number of vibrational modes are incorporated. This upper limit is the Debye frequency  $\omega_D$ . The density of states is found to be given by [Reissland 1972]

$$D(\omega)d\omega = 9N' \omega^2 d\omega / \omega_D^3 \quad (6.13)$$

where  $N'$  is the total number of atoms in the crystal. Using (6.13) in (6.11), and again assuming that  $\langle \delta R(\mu) \delta R(\mu) \rangle$  is independent of  $a$  and  $\mu$ , we find that

$$\langle \delta R(\mu) \delta R(\mu) \rangle = (3\hbar^2 T^2 / 2Mk_B) F(\theta_D/T) \quad (6.14)$$

where the function  $F$  is given by

$$F(u) = \int_0^u X \coth(X/2) dX \quad (6.15)$$

$\theta_D$  is called the Debye temperature, and is given by  $\theta_D = \hbar \omega_D / k_B$ . As in the Einstein model,  $\theta_D$  is usually treated as a parameter, to be chosen so that theory coincides with the relevant experimental data. The problem with the Debye model of course is that it does not correctly describe the optical branches of the phonon spectrum (except for a Bravais lattice, in which there are no such branches). Therefore for our model of the lattice vibrations in GdES, we should use a combination of Debye and Einstein models, describing the acoustic and optical branches respectively. For a lattice of  $N$  unit cells, with  $r$  basis atoms per unit cell, there are  $3N$  acoustic vibrational modes and  $3(r-1)N$  optic vibrational modes (Madeling 1980). Equations (6.12) and (6.14) require slight modifications to allow for the fact that they are incorporating  $3(r-1)N$  and  $3N$  modes respectively. We then arrive at the following approximate result for the thermal average:

$$\begin{aligned} \langle \delta R(\mu) \delta R(\mu) \rangle &= \langle \delta R(\mu) \delta R(\mu) \rangle_a + \langle \delta R(\mu) \delta R(\mu) \rangle_o \\ &= (3 \hbar^2 T^3 / 2 M r k_B \theta_D^3) F(\theta_D / T) \\ &\quad + \hbar / (2 M \omega_o) (1 - 1/r) \coth(\hbar \theta_D / 2 k_B T) \end{aligned} \quad (6.16)$$

We will look at the numerical values of this expression in the next chapter. Before we move on though, a few comments are in order about (6.16). Firstly, although it incorporates all of the modes of the lattice, it does so in a very approximate manner, and the restriction that we must have  $a \ll b$ ,  $\mu \ll \nu$  in (6.9) is a severe one, because the form of the contributions (5.27) and (5.29) shows that we need to consider the cases when  $a \approx b$  and  $\mu \approx \nu$ . Even then one has to assume that the lattice is isotropic in order to get (6.16). None of these problems arise in the Restricted model of the lattice vibrations, for the calculation of the coefficients  $\beta$  in (6.10) is comparatively straightforward. The second point concerns the parameters  $\theta_D$  and  $\omega_o$ . As we have already mentioned, they are usually chosen so that the theory coincides with experiment. The problem with this is that one cannot guarantee that a value of  $\theta_D$  obtained from one matching procedure (e.g. to specific heat data) is applicable to a problem involving a totally diff-

erent set of physical principles. This is what we will have to do here. Since (6.16) is sensitively dependent on  $\theta_0$  and  $\omega_0$ , this is clearly an important point to bear in mind. We will return to equation (6.16) again in chapter seven.

### 6.5 Temperature Dependence of $\mu_{\pm}$

In order to get the expression for  $\mu_{\pm}$  in terms of temperature, and within the Restricted model of lattice vibrations, all that we need do is substitute (6.10) into (5.27) and (5.29). Doing this gives

$$\mu_1 + \mu_2 = \lambda \sum_j A(j) [h/2M\omega_j] \cdot \coth(h\beta h\omega_j/2) \quad (6.17)$$

$$\mu_3 + \mu_4 = \lambda \sum_j C(j) [h/2M\omega_j] \cdot \coth(h\beta h\omega_j/2) \quad (6.18)$$

where the coefficients  $A(j)$  and  $C(j)$  are given by

$$\begin{aligned} A(j) = & \sum_{\mu} \left\{ \sum_{\mu'v} A_{\mu'}(\alpha\mu'v) \cdot \beta_j(\alpha\mu) \beta_j(\alpha v) \right. \\ & + \sum_{\alpha\mu'v} A_{\mu'}(\alpha\mu'v) \cdot \beta_j(\alpha\mu) \beta_j(mv) \\ & + \sum_{\alpha\mu'v} A_{\mu'}(n\mu'v) \cdot \beta_j(m\mu) \beta_j(mv) \\ & \left. + \sum_{\alpha\mu'v} A_{\mu'}(n\mu'v) \cdot \beta_j(n\mu) \beta_j(mv) \right\} \end{aligned} \quad (6.19)$$

$$\begin{aligned} C(j) = & \sum_l \left\{ \sum_{\mu'v} C_l(\alpha\mu'v) \cdot \beta_j(\alpha\mu) \beta_j(\alpha v) \right. \\ & + \sum_{\alpha\mu'v} C_l(\alpha\mu'v) \cdot \beta_j(\alpha\mu) \beta_j(mv) \\ & + \sum_{\alpha\mu'v} C_l(n\mu'v) \cdot \beta_j(m\mu) \beta_j(mv) \\ & \left. + \sum_{\alpha\mu'v} C_l(n\mu'v) \cdot \beta_j(n\mu) \beta_j(mv) \right\} \end{aligned} \quad (6.20)$$

and the coefficient  $\lambda$  was found in chapter three to be given by

$$\lambda = -180/\Delta N^2 N^2$$

From (6.1) the coefficients  $\beta$  are given by

$$\delta R(\mu) = (M)^{-1} \sum_j \beta_j(\mu) Q_j \quad (6.21)$$

where the  $Q_j$  are the normal coordinates of the nine oxygen atoms in the unit cell.

Whilst the forms of (6.17) and (6.18) look comparatively straightforward, one should bear in mind that the electronic coefficients in (6.19) and (6.20) are actually rather complicated functions of the matrix elements of  $X$ ,  $U$  and  $\nabla$ . Their precise form in terms of matrix elements formed from basis functions defined for the static lattice may be found from equations (5.22), (5.24), (5.25), (5.26), (5.28) and (5.30), and they are given in full in appendix A.

## 6.6 Summary and Discussion

In this chapter we have been concerned with the conversion of the contributions to  $\mu_{\text{eff}}$  into a form where the temperature dependence appears explicitly. To do this we considered two models of the lattice vibrations, one in which we consider all of the modes of the lattice, and one in which we consider just the 27 normal coordinates of the oxygen atoms which belong to the water molecules which are nearest neighbours of a given  $\text{Gd}^{3+}$  ion (the Restricted model). Both of these models have their own strengths and weaknesses, but the approximations which lead up to the model for the whole lattice (isotropy,  $a=b$ ,  $\mu=\nu$ , Debye/Einstein models) would seem to be very restrictive in the context of our problem. These approximations are not necessary in the model of the single unit cell, but then it would seem that some error must be incurred by neglecting the rest of the lattice modes. However there are two mitigating factors here: 1) our problem is not concerned with the orbit-lattice interaction; that is, we are not trying to find which modes of the lattice are strongly coupled to the  $\text{Gd}^{3+}$  ion. Our 'effect' arises purely and simply because the mechanism of CEA (chapter three) depends sensitively on the ion/ligand separations, and so might be expected to change if the lattice vibrates. If we were concerned with the orbit-lattice interaction, then clearly we would have to consider all of the modes of the lattice. 2) As we shall see in the next chapter, the nearest neighbouring oxygen atoms are coupled to the rest of the lattice.

ice by means of hydrogen bonds involving the hydrogen atoms belonging to the corresponding water molecules, and the ethylsulphate radicals. The weakness of these bonds suggests that it may not be a bad approximation to assume that the motion of the oxygen atoms in a particular unit cell is largely independent of the motion of the rest of the lattice.

## CHAPTER 7

### Normal Coordinates in the Restricted Model

#### 7.1 Introduction

In this chapter we will calculate the coefficients  $\beta$  and the frequencies  $\omega_j$  which appear in the expressions (6.17) to (6.20), in the Restricted model of lattice vibrations. To do this, we need to obtain the normal coordinates of a complex consisting of nine oxygen atoms (again it is to be assumed that two hydrogen atoms move rigidly with each one), arranged around a stationary  $Gd^{3+}$  ion with  $C_{3h}$  symmetry. In the next section we will briefly outline the general theory of normal coordinates, and in section 7.3 we will consider the nature of the bonding between the various components of the complex. In doing this we will make considerable use of crystallographic data obtained for the ethylsulphates. In section 7.4 we will make use of the bonding information to obtain the potential energy of the lattice when it undergoes a small distortion. From the expression for the potential energy we can construct the force matrix for the system. In section 7.5, the group theoretical properties of the symmetry group of the complex will be used to transform the force matrix into a form which makes the diagonalisation process considerably easier. Finally in section 7.6 we will present the eigenvalues and eigenvectors of the force matrix, thus yielding the frequencies  $\omega_j$ , and the set of coefficients  $\beta$ , respectively.

#### 7.2 The Theory of Normal Coordinates

The calculation of the normal coordinates of an N-particle complex is a very old problem, and the general procedure can be found in most textbooks on classical mechanics, for example Goldstein (1980). The application of group theoretical techniques to the problem is explained very ably in the book by Boardman et al. (1973).

Consider an N-particle complex which is slightly distorted from its position of stable equilibrium. We may write this distortion in the form of a 3N-dimensional vector:



$$\underline{r}_i = \sum_j \underline{r}_{ij} = \sum_j (x_{ij}\underline{x}_j + y_{ij}\underline{y}_j + z_{ij}\underline{z}_j) \quad (7.1)$$

The vector  $\underline{r}_i$  describes the displacement of the  $i^{\text{th}}$  atom in the complex. The unit vectors  $(\underline{x}_j, \underline{y}_j, \underline{z}_j)$  define a local coordinate system centred on the  $i^{\text{th}}$  atom at its equilibrium position, and the  $(x_{ij}, y_{ij}, z_{ij})$  are the coordinates of the  $j^{\text{th}}$  particle with respect to these axes. The choice of coordinate systems for the nine oxygen atoms in our system is shown in figure 7.1. Note that they have been chosen so that they are parallel to the corresponding  $x, y$  and  $z$  axes for which the Hamiltonian  $H_0$  has been defined (equation (5.1)). The coordinates  $x_\mu, y_\mu, z_\mu$  can then be identified with the displacements  $\delta R(\mu)$ ,  $\mu=1,2,3$ , used in previous chapters.

Let us now define column vectors  $|\underline{x}\rangle$  and  $|\underline{y}\rangle$ , along with the corresponding row vectors  $\langle \underline{x}|$  and  $\langle \underline{y}|$ , so that

$$|\underline{x}\rangle = [x_1, y_1, z_1, \dots, x_N, y_N, z_N] \quad (7.2a)$$

$$|\underline{y}\rangle = [y_1, y_1, z_1, \dots, y_N, y_N, z_N] \quad (7.2b)$$

If the complex is vibrating, then in the harmonic approximation the kinetic and potential energies of the complex are quadratic forms, and so may be written as follows:

$$T = \frac{1}{2} \langle \dot{\underline{x}} | \underline{\dot{M}} | \dot{\underline{x}} \rangle \quad (7.3a)$$

$$V = \frac{1}{2} \langle \underline{x} | \underline{K} | \underline{x} \rangle \quad (7.3b)$$

where  $\underline{M}$  and  $\underline{K}$  are the force and mass matrices respectively. The objective of the transformation to normal coordinates is to reduce  $T$  and  $V$  to diagonal form, so that the vibrational Hamiltonian takes the form (6.2). Such a diagonalisation procedure is always possible for a quadratic form [Ayras 1983]. Therefore let us consider a transformation of the coordinates and basis vectors as follows

$$|\underline{q}\rangle = \underline{a}^{-1} |\underline{x}\rangle \quad \text{and} \quad |\underline{q}\rangle = \underline{a}^{-1} |\underline{x}\rangle \quad (7.4)$$

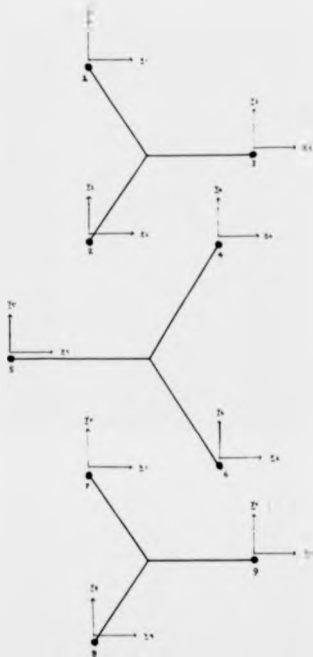


Figure 7.1. The basic vectors used for the calculation of the normal coordinates in the Huxtriated model of lattice vibrations. The places of atoms are viewed by looking vertically down on the cell in fig. 1.2. The vectors  $\xi_1$  to  $\xi_9$  are defined such that  $\xi_i = \xi_1 \pm \xi_i$ . Note that the numbering of the atoms is not the same as that given in fig. 1.2.

where the superscript T denotes the transpose of the  $3N \times 3N$  matrix  $\alpha$ . The last step in (7.4) follows if we insist that the vectors  $q_i$  are normalized so that  $r = (x|q) = (q|q)$ . The kinetic and potential energies now become

$$T = \frac{1}{2} (q|\alpha^T M \alpha|q) \quad (7.5a)$$

$$V = \frac{1}{2} (q|\alpha^T K \alpha|q) \quad (7.5b)$$

If T and V are to become diagonal, then we must choose  $\alpha$  so that

$$\alpha^T M \alpha = I, \quad \alpha^T K \alpha = \text{diag}(\lambda_i) \quad (7.6)$$

where  $\lambda_i$  is equal to  $\omega_i^2$ . That is, the  $K$  matrix is transformed so that its diagonal elements become equal to the vibrational frequencies squared. The vibrational Hamiltonian for the complex then becomes

$$H = \frac{1}{2} \sum_i ( \dot{q}_i^2 + \omega_i^2 q_i^2 ) \quad (7.7)$$

So the general motion of the complex has been reduced to a linear combination of simple harmonic motions. These are called the normal modes of the system. Thus the  $i$ th normal mode of the system corresponds to a distortion of the complex given by  $r = q_i q_i$ , where  $q_i$  defines the pattern of the motion of the atoms in the  $i$ th mode, and  $q_i$  is the  $i$ th normal coordinate, given by  $q_i = q_{i0} \cos(\omega_i t + \epsilon)$ . Note that in general there are only  $3N-6$  non-zero values of  $\omega_i$ , because six degrees of freedom are associated with pure rotations and translations of the complex. The exceptions are linear complexes, and complexes which are constrained in some way.

Comparing equations (6.21) and the second of equations (7.4), we see that the coefficients  $\beta$  are obtained from the elements of the matrix  $\alpha$ . The factor  $M^{-1/2}$  in (6.21) appears by virtue of the first of equations (7.6), which ensures that the elements of  $\alpha$  have dimensions of  $[M]^{-1/2}$ . The problem now is to find  $\alpha$ . With the advent of modern computers, this is now a comparatively straightforward problem, and for many years now programs have been available which not only calculate  $\alpha$ , but also  $K$  and  $M$  too (e.g. see Gwinn (1971)). Alternatively, one can use group theoretical techniques to

exploit the symmetry of the complex (if it has any). It is possible to do this because the  $3N$  basis vectors  $x_1, \dots, x_N$  form a basis for a  $3N$  dimensional reducible representation of the symmetry group, and one of the standard techniques of group theory is the construction of linear combinations of these basis vectors which transform according to the irreducible representations of the symmetry group [Boardman et al. 1973]. These new linear combinations (of which there are a total of  $3N$ ) form the so called 'symmetrized basis', and they often have more convenient properties than the basis vectors  $x_1, \dots, x_N$ , as we shall see shortly. If we write the symmetrized basis vectors as a column vector  $y$ , then we can write

$$y = Y^T x \quad \text{or} \quad x = Y^{-1} y \quad (7.6)$$

The kinetic and potential energies then become

$$T = \frac{1}{2} \langle \dot{y}^T M \dot{y} \rangle = \frac{1}{2} \langle \dot{y}^T \dot{M} \dot{y} \rangle \quad (7.9a)$$

$$V = \frac{1}{2} \langle y^T K y \rangle = \frac{1}{2} \langle y^T K' y \rangle \quad (7.9b)$$

A most important result holds for  $M'$  and  $K'$ , for it may be shown that they are in block form, with one block for each irreducible representation of the symmetry group [Boardman et al. 1973]. The dimension of each block is equal to the number of symmetrized basis vectors transforming according to the corresponding irreducible representation. The advantage of this reduction to block form is that the diagonalisation procedure (7.6) may be carried out for each of the blocks separately, thus drastically reducing the size of the matrices which need to be considered. We note that if  $y$  and  $x$  form mutually orthonormal sets, then  $Y$  is an orthogonal matrix and so the eigenvalues of  $K'$  and  $M'$  are the same as those of  $K$  and  $M$  [Ayres 1983]. Therefore the transformation does not affect the frequencies  $\omega_i$ .

The transformation to normal coordinates now takes the form

$$q = \eta^T y = \eta^T Y^T x \quad (7.10)$$

The matrix  $\underline{\alpha}$  is then equal to  $\underline{\gamma} \underline{\eta}$ . The problem then is to find a matrix  $\underline{\eta}$  such that

$$\underline{\eta}^T \underline{M} \underline{\eta} = \underline{I} \quad \underline{\eta}^T \underline{K} \underline{\eta} = \text{diag}(\lambda_i) \quad (7.11)$$

It may be shown [Boardman et al. 1973] that the following matrix does this

$$\underline{\eta} = \underline{a} \underline{b} \underline{c} \quad (7.12)$$

where  $\underline{a}$  brings  $\underline{M}'$  to diagonal form:  $\underline{a}^T \underline{M}' \underline{a} = \underline{M}''$

$\underline{b}$  reduces  $\underline{M}''$  to the identity:  $\underline{b}^T \underline{M}'' \underline{b} = \underline{I}$

$\underline{c}$  diagonalises  $\underline{b}^T \underline{a}^T \underline{K}' \underline{a} \underline{b}$

This procedure is followed for each block of  $\underline{K}'$  and  $\underline{M}'$ . Hence  $\underline{\eta}$  can be constructed, and so  $\underline{\alpha}$  is found. Because the force matrix  $\underline{K}'$  is in block form, it follows that the matrix  $\underline{\eta}$  will also be in block form, and so a given normal mode  $q_i$  will be equal to a linear combination of symmetrised basis vectors which all transform according to the same irreducible representation. Therefore each normal mode also transforms according to a given irreducible representation. The number of modes which transform according to a given irreducible representation is equal to the number of symmetrised basis vectors belonging to that irreducible representation.

### 7.3 Bonding in GdES

Before we can do any of this, however, we need to calculate the force matrix  $\underline{K}$ , and to do this, we need to know something about the force constants of the bonds between the various components of the complex. The local environment of the  $\text{Gd}^{3+}$  ion in the ethylsulphates has been investigated using crystallographic techniques, among the most recent being the investigations by Albertsson and Elding (1977) and Gherkin and Reppart (1984). Figure 7.2 shows the general structure of the GdES crystal, and figure 7.3 shows in detail the local environment of a  $\text{Gd}^{3+}$  ion, as seen 'from above' (i.e. looking down on the unit cell in figure 1.3). The oxygen atoms lying in the upper and lower triangles in figure 1.3 are lab-

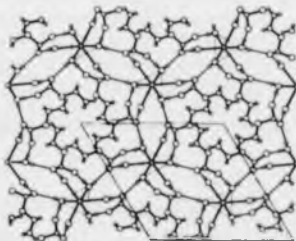


Figure 7.2. The structure of lanthanum ethylsulphate (from Althermann and Biding (1977)). The rhombus marks the crystallographic unit cell, containing two rare-earth ions. The triangles link the oxygen atoms belonging to the upper plane of water molecules in figure 1.3.



Figure 7.3. The local environment of a rare-earth ion in more detail. The view is that which would be seen if we were to look vertically down on the cell shown in fig. 1.2.

elled O(1), and those lying in the central plane are labelled O(2). Those oxygen atoms labelled O(3) and O(5) are involved in hydrogen bonding with the O(1) and O(2) oxygen atoms. The hydrogen atoms associated with the O(1) and O(2) oxygen atoms are labelled H(1) and H(2) respectively. The hydrogen bonds are indicated with a dotted line.

In order to calculate  $K$  we need to know the coordinates of the O(3) and O(5) oxygen atoms, relative to an origin at the centre of the  $Gd^{3+}$  ion. Unfortunately, the two references given above do not provide this information. Instead, they provide a series of bond lengths and angles, from which the various coordinates can be deduced. With the help of some rather tedious trigonometry, we obtain the coordinates shown in table 7.1. The first column indicates the O(1) or O(2) atom also involved in the hydrogen bond. It is assumed throughout that the positions of all of the oxygen atoms and the orientation of all bonds are consistent with the  $C_{3h}$  symmetry of the unit cell. The labelling of the O(1) and O(2) oxygens in table 7.1 is the same as that used in figures 7.1. The lengths are measured in units of  $a_c$ . The coordinates of the O(1) and O(2) oxygens are given in table 1.1.

| Table 7.1: coordinates of the O(3) and O(5) oxygens bonded to the O(1) and O(2) oxygen atoms (in units of $a_c$ ). |             |        |   |             |        |        |
|--|-------------|--------|---|-------------|--------|--------|
| O(1) / O(2) oxygen   | O(3) oxygen |        |   | O(5) oxygen |        |        |
|  | X           | Y      | Z | X           | Y      | Z      |
| 1  | 0.215       | 3.154  | 0 | -3.398      | 1.410  | 0.790  |
| 2  | -2.839      | -1.391 | 0 | 0.477       | -3.648 | 0.790  |
| 3  | 2.624       | -1.763 | 0 | 2.920       | 2.237  | 0.790  |
| 4  | -           | -      | - | 2.690       | 4.659  | 0      |
| 5  | -           | -      | - | -5.380      | 0      | 0      |
| 6  | -           | -      | - | 2.690       | -4.659 | 0      |
| 7  | 0.215       | 3.154  | 0 | -3.398      | 1.410  | -0.790 |
| 8  | -2.839      | -1.391 | 0 | 0.477       | -3.648 | -0.790 |
| 9  | 2.624       | -1.763 | 0 | 2.920       | 2.237  | -0.790 |

The next question we need to answer is how strong are the bonds in the complex. As we have already mentioned, data of this nature does not appear to be available. This is unfortunate, but it is clear from figures 7.2 and 7.3 that we need to consider only two types of bonds, namely the  $Gd - O$  bonds, and the hydrogen bonds between the various oxygen atoms. In particular we notice that there is no direct bonding between pairs of  $O(1)$  or  $O(2)$  oxygen atoms. Therefore, if we assume that contributions to the potential energy arise only as a result of bond stretches (not bond bending), then we need only specify two force constants. Let the force constant for the  $Gd - O$  stretch be  $k$ , and write the force constant for the hydrogen bond stretch as  $\lambda k$ . Spectroscopic data indicates that  $\lambda$  varies from about 0.05 to about 0.2 (Hamilton and Ibers 1968). For convenience, let us put  $\lambda = 0.1$ . We now have only one constant to determine, namely  $k$ . Because of the way that we have defined the hydrogen bond force constant,  $k$  will appear as a factor outside the matrix  $K$ , and so will be a multiplying factor for the normal mode frequencies  $\omega$ . The determination of a value for  $k$  will be deferred until section 7.6.

#### 7.4 The Force Matrix $K$

In order to calculate the force matrix  $K$ , we need to know by how much each bond is stretched when the system undergoes a distortion from its equilibrium position. Throughout the calculation we will assume that the  $O(3)$  and  $O(5)$  oxygen atoms remain stationary. Therefore the bonds stretch purely as a result of the motion of the  $O(1)$  and  $O(2)$  oxygen atoms. Remember that we are assuming that the hydrogen atoms  $H(1)$  and  $H(2)$  move rigidly with the appropriate  $O(1)$  and  $O(2)$  oxygens.

We calculate the bond stretch as follows. Consider a bond of equilibrium length  $a$ . Let one end of the bond be situated at the point  $(a_1, a_2, a_3)$ , and the other end at a point  $(b_1, b_2, b_3)$ . Let the ends suffer displacements  $(x_a, y_a, z_a)$  and  $(x_b, y_b, z_b)$  respectively. The stretch  $\Delta$  which the bond suffers in undergoing these displacements is given by



$$(a+\Delta)^2 = [(a_1-b_1+x_a-x_b)^2 + (a_2-b_2+y_a-y_b)^2 - (a_3-b_3+z_a-z_b)^2] \quad (7.13)$$

If we expand the right hand side of (7.13) and ignore the terms quadratic in displacements, then we easily find that

$$\Delta = [(b_1-a_1)(x_a-x_b) + (b_2-a_2)(y_a-y_b) + (b_3-a_3)(z_a-z_b)]/a \quad (7.14)$$

The increase in potential energy due to this stretch is then just

$$\delta V_{ab} = \frac{1}{2} k \Delta^2 \quad (7.15)$$

where  $k$  is the force constant for the bond stretch. This procedure can be repeated for all pairs of atoms bonded together, and one then arrives at an expression for the total potential energy  $V$ . Once  $V$  has been found, the force matrix  $K$  can be constructed. Because this procedure is algorithmic in nature, we used the computer to obtain  $K$ , with the help of the data in tables 1.1 and 7.1.

The mass matrix  $M$  is somewhat easier to calculate, because

$$T = \frac{1}{2} \sum_i M (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) \quad (7.16)$$

Therefore  $M$  is a diagonal matrix, equal to the identity  $I$  multiplied by  $M$ :

$$\underline{M} = M \underline{I} \quad (7.17)$$

The fact that  $M$  is diagonal is a considerable help in the calculation of  $\alpha$ . This is because if the symmetrized basis vectors ( $\underline{a}$ ) form an orthogonal set, then  $\underline{y}$  is an orthogonal matrix, and so from (7.9) we see that the transformed matrix  $\underline{M}'$  is equal to  $\underline{M}$ . From (7.12) we then see immediately that  $\underline{a} = \underline{I}$ ,  $\underline{b} = M^{-1} \underline{I}$ . That is,  $\underline{a}$  and  $\underline{b}$  take particularly simple forms.

## 7.5 Application of Group Theory

As we have already said, the use of group theory in the normal coordinate problem provides us with considerable assistance, because it allows us to move to a new set of basis vectors  $|a\rangle$ , which, when used in equations (7.9a) and (7.9b), transform the force and mass matrices into new matrices  $K'$  and  $M'$  which are in block form. Each block can then be diagonalised separately. The problem which confronts us now is how do we find the new set  $|a\rangle$ ? The answer lies in the use of group theoretical projection operators (not to be confused with the  $P_a$  of chapter two!). The basis vectors  $|a\rangle$  transform according to the irreducible representations of the symmetry group, and it may be shown that a vector transforming according to the  $\lambda^{\text{th}}$  irreducible representation is given by [Heine 1960]

$$(g_i)_\lambda = \sum_R X_\lambda(R) \cdot R a \quad (7.17)$$

where  $R$  is any element of the symmetry group,  $X_\lambda(R)$  is the character of the element  $R$  in the  $\lambda^{\text{th}}$  irreducible representation, and  $a$  is a vector belonging to the set  $x_1, \dots, x_M$ . Any multiple of (7.17) will also be satisfactory, and so we can choose the set  $|a\rangle$  to be normalized.

The symmetry of the complex which we are considering is  $C_{3h}$ , and the character table is given in table 7.2 below [Heine 1960]. In this table we have defined  $\omega = \exp(2\pi i/3)$ .

| Table 7.2: Character table $X_\lambda(R)$ of $C_{3h}$ |   |            |            |            |             |             |
|---|---|------------|------------|------------|-------------|-------------|
| $\lambda$   | E | $C_3$      | $C_3^2$    | $\sigma_h$ | $S_3$       | $S_3^2$     |
| $A'$  | 1 | 1          | 1          | 1          | 1           | 1           |
| $A''$   | 1 | 1          | 1          | -1         | -1          | -1          |
| $E'$  | 1 | $\omega$   | $\omega^2$ | 1          | $\omega$    | $\omega^2$  |
| $E'$  | 1 | $\omega^2$ | $\omega$   | 1          | $\omega^2$  | $\omega$    |
| $E''$   | 1 | $\omega$   | $\omega^2$ | -1         | $-\omega$   | $-\omega^2$ |
| $E''$   | 1 | $\omega^2$ | $\omega$   | -1         | $-\omega^2$ | $-\omega$   |

In this table,  $\sigma_h$  is a reflection in the mirror plane containing the central triangle of O(1) oxygen atoms, and  $S_2 = \sigma_h C_2$ ,  $S_6^5 = \sigma_h C_3$ . Finally we need to know how many vectors transform according to each irreducible representation of  $C_{3h}$ . The 27 basis vectors  $x_1, \dots, x_{27}$  shown in figure 7.1 form a basis for a 27-dimensional representation of  $C_{3h}$ . Using the standard rules of group theory (Boardman et al. 1973), we can reduce this representation into its irreducible components. If we call the representation  $\Gamma$ , then we find that

$$\Gamma = 5A' \oplus 4A'' \oplus 5E' \oplus 4E'' \quad (7.18)$$

and it follows that we will have five vectors transforming as  $A'$ , four transforming as  $A''$ , ten transforming as  $E'$  and eight transforming as  $E''$ . It also follows from (7.18) and our previous discussions that there will be five normal coordinates transforming as  $A'$ , four as  $A''$ , five doubly degenerate pairs as  $E'$  and four doubly degenerate pairs as  $E''$ .

On applying the formula (7.17), we obtain the results shown in table C1 of appendix C. Once the symmetrized basis (s) has been found, the matrices  $K'$  and  $M'$  can be found. Because we are dealing with large matrices here, the matrix multiplications were done on the computer. As anticipated, we found that  $M' = M$ , and  $K'$  is now in block form. The various blocks are given in tables C2-C5 of appendix C. In order to find the matrix  $\alpha$ , we now apply (7.12) to each block in turn. We have already seen that if the matrix  $y$  is orthogonal, then  $a = I$ ,  $b = M^{-1/2} I$ . Therefore we need to consider the diagonalisation of

$$b^2 a^2 K a b = 1/M K a \quad (7.19)$$

where  $K a$  is the block in  $K'$  which corresponds to the  $\lambda^{th}$  irreducible representation of the  $C_{3h}$  group. The matrix  $\zeta$  which diagonalizes (7.19) is found by obtaining all of the eigenvectors and eigenvalues of (7.19), and then laying out the normalized eigenvectors as the columns of  $\zeta$ . The eigenvalues of (7.19) are the required normal mode frequencies [Ayres 1983]. The matrix  $a$  is then found from  $\eta = a b \zeta$ ,  $\alpha = y \eta$ .

## 7.6 Eigenvalues and Eigenvectors

When the procedure outlined at the end of the previous section is carried through, we obtain the following results for the normal coordinates  $lg$  in terms of the symmetrized basis  $ls$ . Note that six of the normal coordinates were found to have zero frequency. This is a consequence of the fact that the model we used for the bonding between oxygen atoms (ignoring bond bending, retention of only linear terms in (7.14)) allows internal motions of the oxygen atoms which are not resisted by the bonds. The frequencies  $\omega^2$  are multiples of the force constant  $k$  divided by the oxygen mass  $M$ .

Table 7.3: normal modes in terms of the symmetrized basis.

| IRR | g   | $\omega^2$<br>( $\propto k/M$ ) | normal modes ( $\propto M\omega$ )      |
|-----|-----|---------------------------------|---|
| A'  | g1  | 0.092                           | $0.76s_1 + 0.20s_2 - 0.61s_3$           |
|     | g2  | 0.101                           | $-0.14s_1 + 0.98s_2 + 0.14s_3$          |
|     | g3  | 1.007                           | $0.63s_1 - 0.02s_2 + 0.78s_3$           |
|     | g4  | 1.100                           | s4                                      |
| A'' | g5  | 0.092                           | $0.76s_6 + 0.20s_7 - 0.61s_8$           |
|     | g6  | 0.101                           | $-0.14s_6 + 0.98s_7 + 0.14s_8$          |
|     | g7  | 1.007                           | $0.63s_6 - 0.02s_7 + 0.78s_8$           |
|     | g8  | 1.100                           | s9                                      |
| E'  | g9  | 0.092                           | $0.76s_{10} + 0.20s_{11} - 0.61s_{12}$  |
|     | g10 | 0.092                           | $0.76s_{13} + 0.20s_{14} - 0.61s_{15}$  |
|     | g11 | 0.101                           | $-0.14s_{10} + 0.98s_{11} + 0.14s_{12}$ |
|     | g12 | 0.101                           | $-0.14s_{13} + 0.98s_{14} + 0.14s_{15}$ |
|     | g13 | 1.007                           | $0.63s_{10} - 0.02s_{11} + 0.78s_{12}$  |
|     | g14 | 1.007                           | $0.63s_{13} - 0.02s_{14} + 0.78s_{15}$  |
|     | g15 | 1.100                           | s16                                     |
|     | g16 | 1.100                           | s17                                     |
| E'' | g17 | 0.092                           | $0.76s_{20} + 0.20s_{21} - 0.61s_{22}$  |
|     | g18 | 0.092                           | $0.76s_{23} + 0.20s_{24} - 0.61s_{25}$  |
|     | g19 | 0.101                           | $-0.14s_{20} + 0.98s_{21} + 0.14s_{22}$ |
|     | g20 | 0.101                           | $-0.14s_{23} + 0.98s_{24} + 0.14s_{25}$ |
|     | g21 | 1.007                           | $0.63s_{20} - 0.02s_{21} + 0.78s_{22}$  |
|     | g22 | 1.007                           | $0.63s_{23} - 0.02s_{24} + 0.78s_{25}$  |

From the results of tables 7.3 and C1, equations (6.21) and (7.4), we can obtain the coefficients  $\beta$ . These are tabulated in tables 7.4a and 7.4b.

Table 7.4a: the coefficients  $\beta_i(n)$  for  $i=1$  to 11

| n | # | i=1   | i=2   | i=3   | i=4   | i=5   | i=6   | i=7   | i=8   | i=9   | i=10  | i=11  |
|---|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 | 1 | -0.08 | 0.38  | -0.14 | 0     | -0.08 | 0.38  | -0.14 | -0.12 | 0     | 0.53  | 0     |
|   | 2 | 0.31  | 0.15  | 0.22  | 0     | 0.31  | 0.15  | 0.22  | 0.44  | 0     | 0.21  | 0     |
|   | 3 | -0.25 | 0.08  | 0.32  | 0     | -0.25 | 0.08  | 0.32  | -0.35 | 0     | 0.08  | 0     |
| 2 | 1 | -0.23 | -0.32 | -0.18 | 0     | -0.23 | -0.32 | -0.18 | 0.16  | -0.28 | 0.22  | -0.39 |
|   | 2 | -0.23 | 0.25  | -0.23 | 0     | -0.23 | 0.25  | -0.23 | 0.18  | -0.28 | -0.18 | 0.31  |
|   | 3 | -0.25 | 0.08  | 0.32  | 0     | -0.25 | 0.08  | 0.32  | 0.18  | -0.31 | -0.04 | 0.07  |
| 3 | 1 | 0.31  | -0.08 | 0.26  | 0     | 0.31  | -0.08 | 0.26  | -0.22 | -0.38 | 0.04  | 0.07  |
|   | 2 | -0.08 | -0.40 | 0.01  | 0     | -0.08 | -0.40 | 0.01  | 0.08  | 0.10  | 0.28  | 0.49  |
|   | 3 | -0.25 | 0.08  | 0.32  | 0     | -0.25 | 0.08  | 0.32  | 0.18  | 0.31  | -0.04 | -0.07 |
| 4 | 1 | 0     | 0     | 0     | 0.29  | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 2 | 0     | 0     | 0     | 0.50  | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 3 | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
| 5 | 1 | 0     | 0     | 0     | -0.58 | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 2 | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 3 | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
| 6 | 1 | 0     | 0     | 0     | 0.29  | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 2 | 0     | 0     | 0     | -0.50 | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
|   | 3 | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
| 7 | 1 | -0.08 | 0.38  | -0.14 | 0     | 0.08  | -0.38 | 0.14  | -0.12 | 0     | 0.53  | 0     |
|   | 2 | 0.31  | 0.15  | 0.22  | 0     | -0.31 | -0.15 | -0.22 | 0.44  | 0     | 0.21  | 0     |
|   | 3 | 0.25  | -0.08 | -0.32 | 0     | -0.25 | 0.08  | 0.32  | 0.35  | 0     | -0.08 | 0     |
| 8 | 1 | -0.23 | -0.32 | -0.18 | 0     | 0.23  | 0.32  | 0.18  | 0.16  | -0.28 | 0.22  | -0.39 |
|   | 2 | -0.23 | 0.25  | -0.23 | 0     | 0.23  | -0.25 | 0.23  | 0.16  | -0.28 | -0.18 | 0.31  |
|   | 3 | 0.25  | -0.08 | -0.32 | 0     | -0.25 | 0.23  | 0.16  | -0.18 | 0.31  | 0.04  | -0.07 |
| 9 | 1 | 0.31  | -0.08 | 0.26  | 0     | -0.31 | 0.08  | -0.26 | -0.22 | -0.38 | 0.04  | 0.07  |
|   | 2 | -0.08 | -0.40 | 0.01  | 0     | 0.08  | 0.40  | -0.01 | 0.08  | 0.10  | 0.28  | 0.49  |
|   | 3 | 0.25  | -0.08 | -0.32 | 0     | -0.25 | 0.08  | 0.32  | -0.18 | -0.31 | 0.04  | 0.07  |

Table 7.4b: the coefficients  $\beta_i(\mu)$  for  $i=12$  to 21

| $n$ | $\mu$ | $i=12$ | $i=13$ | $i=14$ | $i=15$ | $i=16$ | $i=17$ | $i=18$ | $i=19$ | $i=20$ | $i=21$ |
|-----|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1   | 1     | -0.19  | 0      | 0      | 0      | -0.12  | 0      | 0.53   | 0      | -0.19  | 0      |
|     | 2     | 0.31   | 0      | 0      | 0      | 0.44   | 0      | 0.21   | 0      | 0.31   | 0      |
|     | 3     | 0.45   | 0      | 0      | 0      | -0.35  | 0      | 0.08   | 0      | 0.45   | 0      |
| 2   | 1     | 0.09   | -0.15  | 0      | 0      | 0.16   | -0.28  | 0.22   | -0.39  | 0.09   | -0.15  |
|     | 2     | 0.16   | -0.28  | 0      | 0      | 0.16   | -0.28  | -0.18  | 0.31   | 0.16   | -0.28  |
|     | 3     | -0.23  | 0.39   | 0      | 0      | 0.18   | -0.31  | -0.04  | 0.07   | -0.23  | 0.39   |
| 3   | 1     | -0.16  | -0.31  | 0      | 0      | -0.22  | -0.38  | 0.04   | 0.07   | -0.16  | -0.31  |
|     | 2     | -0.01  | -0.01  | 0      | 0      | 0.06   | 0.10   | 0.28   | 0.49   | -0.01  | -0.01  |
|     | 3     | -0.23  | -0.39  | 0      | 0      | 0.18   | 0.31   | -0.04  | -0.07  | -0.23  | -0.39  |
| 4   | 1     | 0      | 0      | 0.41   | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 2     | 0      | 0      | 0.71   | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 3     | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| 5   | 1     | 0      | 0      | 0.41   | -0.71  | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 2     | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 3     | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| 6   | 1     | 0      | 0      | -0.20  | -0.35  | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 2     | 0      | 0      | 0.35   | 0.61   | 0      | 0      | 0      | 0      | 0      | 0      |
|     | 3     | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      | 0      |
| 7   | 1     | -0.19  | 0      | 0      | 0      | 0.12   | 0      | -0.53  | 0      | 0.19   | 0      |
|     | 2     | 0.31   | 0      | 0      | 0      | -0.44  | 0      | -0.21  | 0      | -0.31  | 0      |
|     | 3     | -0.45  | 0      | 0      | 0      | -0.35  | 0      | 0.08   | 0      | 0.45   | 0      |
| 8   | 1     | 0.09   | -0.15  | 0      | 0      | -0.16  | 0.28   | -0.22  | 0.39   | -0.09  | 0.15   |
|     | 2     | 0.16   | -0.28  | 0      | 0      | -0.16  | 0.28   | 0.18   | -0.31  | -0.16  | 0.28   |
|     | 3     | 0.23   | -0.39  | 0      | 0      | 0.18   | -0.31  | -0.04  | 0.07   | -0.23  | 0.39   |
| 9   | 1     | -0.18  | -0.31  | 0      | 0      | 0.22   | 0.38   | -0.04  | -0.07  | 0.18   | 0.31   |
|     | 2     | -0.01  | -0.01  | 0      | 0      | -0.06  | -0.10  | -0.28  | -0.49  | 0.01   | 0.01   |
|     | 3     | 0.23   | 0.39   | 0      | 0      | 0.18   | 0.31   | -0.04  | -0.07  | -0.23  | -0.39  |

The only problem which remains now is to find a value (or suitable range of values) for the force constant  $k$ . Note that the coefficients  $\beta$  are dimensionless numbers. This follows because from (7.10) and (7.11) we see

that the basis vectors  $q_i$  have dimensions  $[M]^{-1/2}$ , so that the normal coordinates  $q_i$  must have dimensions  $[ML^2]^{1/2}$ . Therefore from (6.21) it follows that the coefficients  $\beta$  must be dimensionless.

## 7.7 Determination of $k$

The usual method of determining the force constants of the various bonds in a molecule is to analyse a Raman spectrum of that molecule. From the spectrum one can determine the vibrational frequencies of the various normal coordinates, and with the help of theory one can then choose the various force constants in a self consistent way [Nakamoto 1986]. To the best of our knowledge, no Raman spectra are available for GdES. Therefore we must choose  $k$  in a different way. Firstly, however, it is worth noting that the normal coordinate frequencies in table 7.3 are all multiples of  $k/M$ , so it is convenient to define a 'characteristic' frequency  $\omega^2 = k/M$ , and to consider the problem of finding a suitable value of  $\omega$  instead. To choose  $\omega$ , we will use the ideas of the previous chapter, and attempt to match the values of  $\langle \delta R(\mu) \delta R(\mu) \rangle$  obtained using the Debye/Einstein models with those obtained using the Restricted model. That is, we will require that

$$\sum_{\mu} \langle \delta R(\mu) \delta R(\mu) \rangle_{\text{Debye}} = \sum_{\mu} \langle \delta R(\mu) \delta R(\mu) \rangle_{\text{RES}} \quad (7.20)$$

The right hand side of (7.20) can be obtained from (6.10), using the fact that the coefficients  $\beta$  satisfy the orthogonality relation

$$\sum_{\mu} \beta_j(\mu) \beta_{j'}(\mu) = \delta_{jj'} \quad (7.21)$$

This relation follows from the fact that the normal modes  $q_i$  satisfy the orthogonality relation  $q_i \cdot q_{i'} = 1/M \delta_{ii'}$ , because of the way they are constructed. Equation (7.21) also, of course, follows from (6.3) when  $N=1$ . To calculate the left hand side of (7.20), we need to find the Debye temperature  $\theta_D$  of GdES. In the literature one can find several values. For instance, it is found that spin-lattice relaxation data for GdES can be explained well if we take  $\theta_D=65K$  [Krygin et al. 1981]. On the other hand, specific heat data may be accounted for using a combination of Debye and

Einstein models with a Debye temperature of  $\theta_D=155\text{K}$  [Papoular 1962]. If the internal motion of the ethylsulphate radicals and the water molecules is ignored (as in our model), then one finds that  $\theta_D=167\text{K}$  [McColl 1988]. In table 7.5, the results of performing the matching procedure (7.20) are shown for all three values of  $\theta_D$ , as a function of temperature. The left hand side of (7.20) is obtained from equation (6.16), with  $r=0$ . We were unable to find any data relating to the Einstein frequency of GdES, and so for simplicity we assumed that the Einstein and Debye frequencies were equal. The values of  $\omega$  in table 7.5 were chosen so that the sum of the squares of the differences of the left and right hand sides of (7.20) were a minimum. The thermal averages are measured in units of  $a_0^3$ .

| Table 7.5: comparison of the left and right hand sides of (7.20) for various $\theta_D$ and $\omega$ ( $\times 10^{13} \text{ s}^{-1}$ ). The units are $a_0^3$ |                       |               |                        |               |                        |               |
|---|-----------------------|---------------|------------------------|---------------|------------------------|---------------|
| T / K   | $\theta_D=65\text{K}$ | $\omega=1.70$ | $\theta_D=155\text{K}$ | $\omega=4.04$ | $\theta_D=167\text{K}$ | $\omega=4.35$ |
| 10  | 2.140                 | 1.779         | 0.878                  | 0.728         | 0.817                  | 0.676         |
| 50  | 4.131                 | 4.035         | 1.027                  | 0.931         | 0.934                  | 0.835         |
| 90  | 6.915                 | 6.875         | 1.401                  | 1.355         | 1.243                  | 1.191         |
| 130   | 9.820                 | 9.795         | 1.857                  | 1.834         | 1.629                  | 1.596         |
| 170   | 12.731                | 12.740        | 2.341                  | 2.334         | 2.045                  | 2.026         |
| 210   | 15.568                | 15.697        | 2.833                  | 2.843         | 2.470                  | 2.463         |
| 250   | 18.459                | 18.659        | 3.347                  | 3.358         | 2.902                  | 2.905         |
| 290   | 21.505                | 21.624        | 3.849                  | 3.876         | 3.342                  | 3.351         |

It will be noticed that for these choices of  $\omega$ , the agreement between the values obtained with the Restricted model and those obtained using the Debye/Einstein models is good throughout the whole temperature range.

In section 6.3 of chapter six we made the point that the Debye model of lattice vibrations is only really valid for the approximation of the acoustic modes of the lattice, and similarly that the Einstein model is a good approximation only for the optical modes. To illustrate this point we have calculated  $\langle RR(\omega) \rangle$  using the Debye model (equation (6.14)) and



the combined Debye + Einstein model (equation (8.16)), as a function of temperature. The results from the two models are compared in table 7.6.

| T / K | Table 7.6: calculation of $\langle \delta R(\mu) \delta R(\mu) \rangle$ using the Debye and Debye/Einstein models (in units of $\text{\AA}^2$ ) |       |                        |       |                        |       |
|-------|---|-------|------------------------|-------|------------------------|-------|
|       | $\theta_D=65\text{K}$   |       | $\theta_D=155\text{K}$ |       | $\theta_D=167\text{K}$ |       |
|       | D+E   | D     | D+E                    | D     | D+E                    | D     |
| 10    | 0.079   | 0.216 | 0.033                  | 0.080 | 0.030                  | 0.074 |
| 50    | 0.153   | 0.596 | 0.038                  | 0.126 | 0.035                  | 0.111 |
| 90    | 0.256   | 1.045 | 0.052                  | 0.196 | 0.046                  | 0.171 |
| 130   | 0.364   | 1.472 | 0.069                  | 0.272 | 0.060                  | 0.235 |
| 170   | 0.471   | 1.947 | 0.087                  | 0.350 | 0.076                  | 0.303 |
| 210   | 0.577   | 2.342 | 0.105                  | 0.426 | 0.091                  | 0.369 |
| 250   | 0.684   | 2.764 | 0.124                  | 0.502 | 0.107                  | 0.435 |
| 290   | 0.796   | 3.272 | 0.143                  | 0.585 | 0.124                  | 0.504 |

In table 7.6 it will be noticed that the agreement between the values for  $\langle \delta R(\mu) \delta R(\mu) \rangle$  obtained using a simple Debye model and those obtained using a combined Debye/Einstein model is poor. In fact, for  $\theta_D=65\text{K}$ , the simple Debye model predicts a root-mean square amplitude of about 1.8  $\text{\AA}$ . at 290K. This is about forty percent of the equilibrium bond length ( $\sim 4.5 \text{\AA}$ ), and as such has got to be considered too large. The discrepancy between the two sets of values arises, of course, because the Debye model does not correctly describe the optical phonon modes. It should also be remembered that we have ignored anharmonic effects throughout the calculation.

## 7.8 Summary and Discussion

In this chapter we have concentrated solely on the calculation of the normal coordinates of a complex consisting of the nine oxygen atoms which are involved in the excitation process contributing to  $\mu_{\text{vib}}$ . From these coordinates we obtained the coefficients  $\beta$  listed in table 7.4. The main

problems we encountered were concerned with the nature of the bonding between the various components of the complex. Whilst a qualitative picture could be obtained from crystallographic work, quantitative values for the strength of the bonds could not. Therefore we defined a force constant  $k$  for the  $Gd - O(\xi)$  bonds, and wrote the hydrogen bond strength as  $\lambda k$ , with  $\lambda = 0.1$ . In fact, provided  $\lambda$  is small ( $0.05 \leq \lambda \leq 0.2$ ), we find that our results are not significantly affected by a change in  $\lambda$ . This then leaves us with the problem of finding  $k$ . It was decided that the best way to try and do this would be to try and match the values of  $\langle R(\mu) R(\mu) \rangle$  obtained with the Restricted model to those values obtained with the Debye/Einstein model. This procedure is complicated by the fact that in the literature there are at least three different estimates of  $\theta_D$  for the rare-earth ethylsulphates. We have therefore obtained three different estimates of  $k$  (via a characteristic frequency  $\omega$ ). We will not attempt to choose between these values at this stage; instead we will present the final results for  $\mu_k$  for all three cases.

## CHAPTER 8

### Evaluation of Electronic Coefficients

#### 8.1 Introduction

In chapters six and seven we focused all of our attention on the lattice vibrational parts of the problem. In this chapter and the next we will concentrate on the calculation of the electronic coefficients which appear in equations (6.19) and (6.20). Their exact forms are given in appendix A, and so what we need to do is to evaluate them, and tabulate them as functions of their respective parameters (e.g.  $\alpha, m, \mu, v$  etc.), and then substitute them back into (6.19) and (6.20) along with the  $\beta$  coefficients which we calculated in chapter seven. The sheer complexity of this problem means that both the evaluation of the electronic coefficients and the summations must be done on the computer. In this chapter we will examine the technical aspects of the problem. In section 8.2 we will discuss the choice of basis functions which were used in the calculation, in particular the choice for the  $3s$ -orbital on one of the neighbouring oxygen atoms, which is slightly different from that used in chapter three. In chapter five we made a series of approximations in the formulation of the problem, in an effort to reduce the algebraic complexity of the final expression for  $\mu_{\nu\lambda}$ . However, it can be seen that the expressions in appendix A are still quite complex, and as such they will be very time consuming to evaluate. In section 8.3 we will introduce some more approximations in an attempt to make the numerical calculation more tractable. In sections 8.4 and 8.5 we will describe the algebraic techniques required to evaluate the one-body and two-body matrix elements, respectively. We will defer the numerical evaluation of these quantities to the next chapter. In that chapter we will also make a more rigorous estimate of the energy denominator  $\Delta$ .

#### 8.2 Basis Functions

In choosing the basis functions which we are going to use to evaluate the expressions in appendix A, we will follow the ideas of CEA in chapter three and approximate the Wannier functions of the Method of Stevens with

simple atomic-like orbitals (i.e. functions equal to a radial wavefunction multiplied by a spherical harmonic). The advantage of doing this is that atomic orbitals are generally easier to work with than Wannier functions. However, there is a corresponding disadvantage. Because atomic orbitals are defined for a free (isolated) ion, it follows that two orbitals situated on different sites will not in general be orthogonal, even though all atomic orbitals centred on the same site will be mutually orthogonal. This is inconvenient, because the Method of Stevens requires all of the basis functions to be mutually orthonormal. This of course is a characteristic property of Wannier functions (see appendix D). For the moment though, we will ignore this difficulty.

Let us then define an atomic 4f-orbital  $|4f\rangle$ , centred on the  $Gd^{3+}$  ion, and characterized by a magnetic quantum number  $m$ . Let us also define functions  $|1aR\rangle$ ,  $|2sR\rangle$ ,  $|2pRm_p\rangle$  and  $|3aR\rangle$ , which are atomic orbitals centred on an oxygen atom at a position vector  $R$  relative to the  $Gd^{3+}$  ion.  $m_p$  is the magnetic quantum number of the  $2p$ -function. Note that we do not need to include spin wavefunctions in these basis states, because the spin of the states has already been incorporated in moving from the second quantized operators to the SCCF operator. The basis states are of the form

$$|4f\rangle = \psi_{4f}(r) Y_3^m(\Omega) \quad (8.1a)$$

$$|1aR\rangle = \psi_{1a}(r') Y_0^0(\Omega') \quad (8.1b)$$

$$|2sR\rangle = \psi_{2s}(r') Y_0^0(\Omega') \quad (8.1c)$$

$$|2pRm_p\rangle = \psi_{2p}(r') Y_1^{m_p}(\Omega') \quad (8.1d)$$

$$|3aR\rangle = \psi_{3a}(r') Y_0^0(\Omega') \quad (8.1e)$$

In equations (8.1a) to (8.1e), the variables  $\Omega$  and  $\Omega'$  denote the angular variables  $\theta, \phi$  and  $\theta', \phi'$  respectively. The variables  $r', \theta'$  and  $\phi'$  are defined with respect to axes centred on the oxygen atom at position vector  $R$ . We now need to choose radial wavefunctions for the orbitals in (8.1). For the 4f-functions we will follow CEA, and use the radial wavefunction of Freeman and Watson (1962). The wavefunction and its parameters are given in chapter three. For the 1s, 2s and 2p-oxygen wavefunctions, we will use

the simple Slater orbitals. They have the advantage that they are easy to work with, and they provide a reasonable approximation to the true atomic wavefunction for large values of  $r'$  (i.e. where the overlap with the 4f-functions is likely to be greatest). They can be written in the following general form:

$$\Psi(r) = N r^n \exp[-(\sigma)r/a_0] \quad (8.2)$$

where  $N$  is a normalization constant, and  $n$  and  $\sigma$  are to be determined. Following the usual rules for obtaining these quantities (Griffiths 1962), we obtain the following expressions for the required orbitals:

$$\Psi_{1s}(r') = 42.02/a_0^{3/2} \exp[-7.7r'/a_0] \quad (8.3a)$$

$$\Psi_{2s}(r') = 9.014/a_0^{3/2} r' \exp[-2.275r'/a_0] \quad (8.3b)$$

$$\Psi_{2p}(r') = 9.014/a_0^{3/2} r' \exp[-2.275r'/a_0] \quad (8.3c)$$

For the 3s-function we will follow CEA and choose one of hydrogenic form, with two nodes. That is, we will take

$$\Psi_{3s}(r') = A(4A)^3 [1-2Ar'+2/3(Ar')^2] \exp(-Ar') \quad (8.4)$$

In this expression,  $A$  is a parameter, with dimensions  $a_0^{-1}$ , which is to be determined. Our next problem is to ensure that all of the basis functions (8.1) are mutually orthogonal. The 2p-functions are clearly orthogonal to the s-functions on the same oxygen atom, but it is not clear that the s-functions chosen in this way are mutually orthogonal, nor is it clear that the 4f-functions are orthogonal to the oxygen wavefunctions. In addition, it is unlikely that the oxygen wavefunctions on different sites will be mutually orthogonal. Because the 1s, 2s and 2p-functions are fairly tightly bound to the oxygen atom, we will assume that they are orthogonal to the 4f-functions on the  $Gd^{3+}$  ion, because the 4f-functions themselves are fairly tightly bound. We will also assume that the 1s, 2s and 2p-functions on a given oxygen atom are orthogonal to the 1s, 2s and 2p-functions on all of the other oxygen atoms. This leaves us with the problem of the 3s-functions. In general, a 3s-function will not be orthogonal to the other

s-functions on the same site. In addition, it will not in general be orthogonal to the 4f-functions, nor will it be orthogonal to functions centred on the other oxygen atoms. This presents us with a real problem, because (8.4) contains only one parameter, and so we cannot expect to satisfy all of the orthogonality criteria in a simple way. CEA circumvented this problem by choosing A so as to make (8.1a) as close as possible to being orthogonal to the 1s and 2s-functions on the same oxygen site. They then used the procedure of Lowdin to ensure that the 3s-functions are orthogonal to the 4f-functions, the result being a new set of 'orthogonalized' orbitals (3.26a) and (3.26b). The fact that the 3s-orbitals are not orthogonal between sites is of no great importance, because CEA have shown that incorporating these overlaps in a Lowdin procedure does not lead to appreciable corrections to the matrix elements, even though the overlaps are not small enough to neglect "a priori" ( $\langle 3sR|3sR' \rangle = 0.1$ ).

Towards the end of chapter three we noted that the use of a Lowdin procedure to ensure orthogonality between the 3s and 4f-functions leads to a considerable increase in the algebraic complexity of the problem. This increase in complexity would become very severe for our problem, for a study of appendix A shows that we have over 200 terms to evaluate to find  $\mu_{\text{eff}}$ , as opposed to the 4 terms required to find  $\mu_{\text{eff}}$  in chapter three. In general, the terms are rather more complicated too. It would therefore be desirable to find a different way of satisfying the orthogonality requirements, so that we are left with a tractable numerical calculation. CEA have shown that the most important corrections arise from orthogonalizing the 3s and 4f-functions, so we will choose the parameter A so that these orbitals are automatically orthogonal. That is, we will insist that  $\langle 4f|3sR \rangle = 0$ . Using (8.1), (8.4) and the techniques of appendix B, this leads to

$$\int \psi_{4f}(r) \phi(3s, r, R) r^2 dr = 0 \quad (8.5)$$

where we have defined a new quantity

$$g(1,r,R) = (4\pi)^{-3/2} A(4A)^{-3/2} [a_1(0,r,R) - 2Aa_1(1,r,R) + 2/3A^2a_1(2,r,R)] \quad (8.6)$$

Evaluation of (8.5) leads to the following values of A:

$$\begin{aligned} \text{O(1) atom: } R &= 4.4785a_0 \quad \bullet \quad A = 1.5205a_0^{-1} \\ \text{O(2) atom: } R &= 4.7619a_0 \quad \bullet \quad A = 1.4161a_0^{-1} \end{aligned} \quad (8.7)$$

We will discuss the merits and failings of this approach at the end of the chapter. The overlap of these 3s-functions with the 1s and 2s-functions on the same site are given by

$$\begin{aligned} \text{O(1) atom: } \langle 1sR|3sR \rangle &= 0.092 \quad \langle 2sR|3sR \rangle = -0.064 \\ \text{O(2) atom: } \langle 1sR|3sR \rangle &= 0.098 \quad \langle 2sR|3sR \rangle = -0.105 \end{aligned}$$

These overlaps are fairly small, and so it is possible to orthogonalize the 3s-functions to the 1s and 2s-functions on the same site with the help of Lowdin's procedure. Consider for instance the two-body matrix element  $\langle m_1, m_2 | U | 3sR, m_3 \rangle$ . It can easily be shown that the use of Lowdin's procedure leads to corrections involving matrix elements like  $\langle m_1, m_2 | U | 1sR, m_3 \rangle$  and  $\langle m_1, m_2 | U | 2sR, m_3 \rangle$ , multiplied by  $W(1sR|3sR)$  and  $W(2sR|3sR)$  respectively. As we shall see later, these two-body matrix elements are small, and since these overlaps are also small, it follows that Lowdin's procedure will introduce only small corrections to  $\langle m_1, m_2 | U | 3sR, m_3 \rangle$ . For the sake of simplicity, we will ignore these corrections.

### 8.3 Assumptions and Approximations

We now have approximations to all of the basis functions which we need to evaluate the matrix elements in appendix A. But in spite of the way in which we chose them (particularly the way we have satisfied the orthogonality requirements), we are still left with a formidable computational exercise. Therefore we would like to make a few more simplifications, if possible. One way we could do this is to try and eliminate those terms

from appendix A which are small, compared with the largest terms in appendix A. To do this we begin by noting that many of the matrix elements which appear involve the product of two wavefunctions which are centred on different sites in the system. We will refer to such a product as an "off-site overlap". Because the size of a matrix element is determined by the extent of the overlap of its constituent wavefunctions, it follows that a matrix element containing an off-site overlap is likely to be smaller than a matrix element which involves a product of wavefunctions centred on the same site. It then further follows that the terms in appendix A whose constituent matrix elements contain the greatest number of off-site overlaps are also likely to be the smallest numerically. We will therefore neglect all terms in appendix A which contain four or more off-site overlaps. We choose four off-site overlaps as the cut-off point because this removes all terms which involve exchange-like integrals, and these can easily be demonstrated to be small. For instance, consider the matrix element

$$\langle m_1, 3aR | U | 3aR, m_2 \rangle$$

To evaluate this, we need (8.1a), (8.1e), (8.4), (8.6) and the following result for the expansion of  $|r_1 - r_2|^{-1}$  into spherical harmonics [Mathews and Walker 1983]:

$$|r_1 - r_2|^{-1} = \sum_{kq} \lambda(k) f(r, k) Y_k^q(\hat{r}_1) Y_k^q(\hat{r}_2) \quad (8.8)$$

where we have defined the following quantities:

$$f(r, k) = \frac{r^k}{r^{k+1}} \quad \text{and} \quad \lambda(k) = 4\pi/2k+1$$

In this expression,  $r_1$  and  $r_2$  are the lesser and greater of the variables  $r_1$  and  $r_2$ , respectively. The exchange-like matrix element is then found to be given by

$$\begin{aligned} & \sum_{L_1} \sum_{L_2} \iint \Psi_{L_1}(r_1) \Psi_{L_2}(r_2) P(r, k) \Psi_{L_1}(r_1) \Psi_{L_2}(r_2) r_1^3 r_2^3 dr_1 dr_2 \\ & \times \lambda(L_1) \lambda(L_2) Y_{L_1}^m(R) Y_{L_2}^m(R) U(3, m_1, k, q, l, m) U(L, R, k, q, 3, m_2) \end{aligned} \quad (8.9)$$



In this expression  $Y_L^M(R)$  denotes a spherical harmonic evaluated at the  $\theta$  and  $\phi$  coordinates which define the orientation of the vector  $R$ . We have also defined the following new quantity:

$$U(a, d, b, e, c, f) = \int Y_a^d(\Omega) Y_b^e(\Omega) Y_c^f(\Omega) d\Omega \quad (8.10)$$

In (8.10), a bar over the magnetic quantum number indicates that the spherical harmonic to which it refers is complex conjugated in the integral. The integral is easily evaluated, and is given by [Rotenberg et al 1959]

$$(-1)^d (4\pi)^{-3/2} [(2a+1)(2b+1)(2c+1)]^{-1/2} \begin{bmatrix} a & b & c \\ -d & e & f \end{bmatrix} \begin{bmatrix} a & b & c \\ 0 & 0 & 0 \end{bmatrix} \quad (8.11)$$

The last two quantities in (8.11) are 3j-symbols, and the rules for coupling the ranks [Rotenberg et al p2] define the allowed values of  $L, l$  and  $k$  in (8.9). The sizes of the appropriate radial integrals then determine the magnitude of the matrix element. If we write the radial integral in the abbreviated form  $R(k, l, L)$ , then the largest ones are found to be

$$\begin{aligned} R(1, 1, 2) &= 6 \times 10^{-5} \text{ a}^2/\text{a}_0 & R(2, 1, 1) &= 3 \times 10^{-4} \text{ a}^2/\text{a}_0 \\ R(1, 0, 0) &= 2 \times 10^{-4} \text{ a}^2/\text{a}_0 & R(4, 1, 1) &= 2 \times 10^{-4} \text{ a}^2/\text{a}_0 \end{aligned}$$

Therefore we can expect the exchange matrix elements to have a magnitude of between about  $10^{-3} \text{ a}^2/\text{a}_0$  and  $10^{-4} \text{ a}^2/\text{a}_0$ . This should be compared with the corresponding direct integral  $\langle m_1, 3sR|U|m_2, 3sR \rangle$ , which from a simple classical argument can be expected to have a magnitude of about  $\text{a}^2/2R$ , i.e. around  $0.11 \text{ a}^2/\text{a}_0$ , when  $m_1 = m_2$ . Therefore we are well justified in ignoring the exchange-like matrix elements. When the exchange matrix elements involve  $1s, 2s$  or  $2p$ -functions, we can expect the disparity between the direct and exchange matrix elements to be even greater, because these functions are more strongly localized about the oxygen atom than the  $3s$ -functions. Therefore the exchange matrix elements will be even smaller, and the approximation of ignoring them even better.

The second approximation that we want to make concerns the  $1s$ -orbitals. All of the terms in appendix A contain one or more matrix elements of the

form  $\langle m|O|laR\rangle$ , where the operator  $O$  is either  $X, \nabla$  or some combination of the two. The extreme localized character of (8.3a) means that these matrix elements are an order of magnitude or more smaller than the same matrix elements with  $2s, 2p$  or  $3s$ -functions (we have checked this). Two-body Matrix elements of the form  $\langle m_1, m_2|U|laR, m_3\rangle$  are entirely negligible, for the largest radial integrals are found to be around  $10^{-6} \text{ a.u.}$ . We will therefore drop all of the  $1s$ -functions from our basis set, on the grounds that their inclusion would make little difference to the order of magnitude (and perhaps more importantly the sign) of the final result.

#### 8.4 Evaluation of One-Body Matrix Elements

In this section we will consider the evaluation of the one-body matrix elements which appear in appendix A. Before we do this, though, it is useful to note that each one-body matrix element belongs to one of eight distinct categories. Let  $|a\rangle$  and  $|\beta\rangle$  represent orbitals centred on any two of the nine oxygen neighbours. The eight categories are

|                                    |  |        |
|------------------------------------|--|--------|
| a) $\langle a X m\rangle$          | e) $\langle a X \beta\rangle$          |        |
| b) $\langle a \nabla_u m\rangle$   | f) $\langle a \nabla_u \beta\rangle$   | (8.12) |
| c) $\langle a X\nabla_u m\rangle$  | g) $\langle a X\nabla_u \beta\rangle$  |        |
| d) $\langle a \nabla_u X m\rangle$ | h) $\langle a \nabla_u X \beta\rangle$ |        |

Once these matrix elements have been evaluated, all other one-body matrix elements may be obtained from them, using the relation [Schiff 1968]

$$\langle a|O|b\rangle = \langle b|O^\dagger|a\rangle^*$$

In order to evaluate the matrix elements in (8.12), we need to consider the action of the various operators on the basis states (8.1). To find the action of the gradient operator  $\nabla$  it is convenient to use the spherical components  $\nabla_1, \nabla_0$  and  $\nabla_{-1}$ . These are defined as follows [Edmonds 1958]:

$$\begin{aligned}
\psi_x &= 1/2 [\psi_{-1} + \psi_1] \\
\psi_y &= 1/2 [\psi_{-1} - \psi_1] \\
\psi_z &= \psi_0
\end{aligned}
\tag{8.13}$$

The following result then holds [Varshelovich 1980]

$$\begin{aligned}
\psi_a [R(r)Y_n^m(\Omega)] &= A(l, m, a) [R' - (R/r) Y_{l+1}^{m+1}] \\
&+ B(l, m, a) [R' + (l+1)R/r] Y_{l-1}^{m-1}
\end{aligned}
\tag{8.14}$$

where, for convenience, we have omitted the dependent variables  $r$  and  $\Omega$ , and  $R' = dR/dr$ . The coefficients  $A$  and  $B$  are given by

$$\begin{aligned}
A(l, m, 0) &= [(l+1)^2 - m^2]^{1/2} / P \\
B(l, m, 0) &= [l^2 - m^2]^{1/2} / P \\
A(l, m, -1) &= [(l-m+1)(l-m+2)]^{1/2} / P/2 \\
B(l, m, -1) &= [(l+m+1)(l+m)]^{1/2} / P/2 \\
A(l, m, 1) &= [(l+m+1)(l+m+2)]^{1/2} / P/2 \\
B(l, m, 1) &= [(l-m-1)(l-m)]^{1/2} / P/2
\end{aligned}
\tag{8.15}$$

where  $P$  is given by

$$P = [(2l+1)(2l+3)]^{1/2}$$

The operator  $X$  is defined in equation (3.10). From equation (1.31) in Rotenberg et al (1959) we find that

$$\begin{aligned}
X [R(r)Y_n^m(\Omega)] &= (-\hbar^2/2m [R'' + 2R'/r - l(l+1)R/r^2] \\
&- Z_0^2 e^2 R/r) Y_n^m
\end{aligned}
\tag{8.16}$$

From equations (8.13) to (8.16) we then obtain the following results

$$\nabla_a |m\rangle = A(3,m,a) [\nabla_{4r} - 3/r\nabla_{4r}] Y_4^{m,a} \quad (8.17a)$$

$$+ B(3,m,a) [\nabla_{4r} + 4/r\nabla_{4r}] Y_2^{m,a}$$

$$\nabla_a |naR\rangle = A(0,0,a) [\nabla_{a0}] Y_1^0 \quad (8.17b)$$

$$X |m\rangle = (-\hbar^2/2m [\nabla_{4r}^2 + 2/r\nabla_{4r} - 12/r^2\nabla_{4r}] \quad (8.17c)$$

$$- Z_0^2 e^2/r \nabla_{4r}) Y_3^m$$

$$X |naR\rangle = (-\hbar^2/2m [\nabla_{a0}^2 + 2/r\nabla_{a0}] - Z_0^2 e^2/(R-R) \nabla_{a0}) Y_0^0 \quad (8.17d)$$

$$\begin{aligned} \nabla_a \nabla_b |naR\rangle = & A(0,0,a) \{A(1,a,b) [\nabla_{a0}^2 - 1/r\nabla_{a0}] Y_2^{a+b} \\ & + B(1,a,b) [\nabla_{a0}^2 + 2/r\nabla_{a0}] Y_0^{a+b}\} \end{aligned} \quad (8.17e)$$

The action of the operators  $X\nabla_a$  and  $\nabla_a X$  can be obtained in the same way. However the calculation is rather tedious, and so we will not quote the results here. In (8.17d) we have transferred the origin of coordinates to the centre of the oxygen atom at R, hence the form of the last term in that expression. The kinetic energy operator is of course unchanged.

From these expressions we are now able to obtain all of the one-body matrix elements which appear in appendix A. There is, however, another slight complication. The one-body matrix elements may be split up into two further categories, depending on whether they are "two-centre" or "single-centre" integrals. Any element which contains a  $4f$ -function will always be a two-centre integral, and is evaluated with the help of the techniques of appendix B. Any matrix element containing two oxygen wavefunctions may be either a single centre or a two-centre integral. If it is single centre, the evaluation is trivial. If it is a two-centre integral, then the techniques of appendix B are used.

As an example of how we calculate two-centre, one-body integrals, let us consider the matrix element  $\langle a|X|m\rangle$ . We need to consider two distinct cases: 1)  $|a\rangle$  is an  $s$ -function, and 2)  $|a\rangle$  is a  $p$ -function. For the first case let us assume that  $|a\rangle$  is a  $2s$ -function. Bearing in mind that the  $4f$ -

functions (see equation (3.24) and table 3.1) have dimensions of  $a_0^{-3/2}$ , all lengths being measured in units of  $a_0$ , we see from (8.17) and (8.3) that the kinetic energy part of  $X$  will give a contribution which is a multiple of  $\hbar^2/ma_0^2$ , and the potential energy part will give a term which is a multiple of  $a^2/a_0$ . Because  $a_0 = \hbar^2/ma^2$  (in Gaussian units), it follows that we may measure the magnitude of the matrix elements of  $X$  in units of  $a^2/a_0$ , the multiplying factor being given by the matrix elements of

$$X' = -\frac{1}{2} \nabla^2 - \frac{Z_0^2}{r} \quad (8.18)$$

between wavefunctions with  $a_0$  set equal to unity (atomic units). Note that the operator  $X'$  is now dimensionless. To evaluate the matrix element, we use equation (B8) to rewrite the s-function in terms of coordinates centred on the  $Gd^{3+}$  ion. Performing the angular integrals then gives

$$\begin{aligned} \langle 2sR|X|s \rangle &= C a^2/a_0, \\ C &= 2.578 \lambda(3) Y_0^0(R) \int a_3(1,r,R) [-\frac{1}{2} \nabla^2 - \frac{Z_0^2}{r}] \psi_{4f}(r) r^2 dr \end{aligned} \quad (8.19)$$

where  $r$  is measured from the  $Gd^{3+}$  ion. Remember that  $C$  is to be evaluated with  $a_0$  set equal to unity in the wavefunctions.

To evaluate the matrix element  $\langle 2pR|X|s \rangle$ , we use the same arguments, except that equation (B12) is used instead of (B8) to rewrite the p-function in terms of coordinates centred on the  $Gd^{3+}$  ion. We then obtain the following result, with the help of (8.3c) and the relation  $Y_1^0 = (-1)^M Y_1^{-M}$

$$\begin{aligned} \langle 2pR|X|s \rangle &= C a^2/a_0, \\ C &= 9.014 \lambda(3) Y_1^0(R) Y_0^0(R) \int R a_3(0,r,R) [-\frac{1}{2} \nabla^2 - \frac{Z_0^2}{r}] \psi_{4f}(r) r^2 dr \\ &+ 9.014 \lambda(2) (-1)^M U(1,0_0,2,-M,3,M) Y_2^M(R) R(2,r,R) \\ &+ 9.014 \lambda(4) (-1)^M U(1,0_0,4,-M,3,M) Y_4^M(R) R(4,r,R) \end{aligned} \quad (8.20)$$

where we have defined

$$R(l,r,R) = \int a_3(1,r,R) [-\frac{1}{2} \nabla^2 - \frac{Z_0^2}{r}] \psi_{4f}(r) r^2 dr \quad (8.21)$$

Again all wavefunctions are evaluated with  $a_0$  set to unity. The functions  $U$  are defined in (8.10) and (8.11).  $M$  is given by  $-M-m_0+m = 0$ .

If the same dimensional arguments are applied to the other one-body matrix elements, then we find that the matrix elements of  $\nabla$  are measured in units of  $1/a_0$ , and those of  $X\nabla$  and  $\nabla X$  are measured in units of  $a_0^2/a_0^3$ . These "extra" factors of  $1/a_0$  are cancelled by the displacements  $\delta R$  which we have considered in the previous two chapters.

### 8.5 Evaluation of Two-Body Matrix Elements

The evaluation of the two-body matrix elements is in many ways no more difficult than the evaluation of the one-body elements, because we do not require any new analytical techniques. If we consider the dimensions of the matrix elements of  $U$ , then we find that they are energies, measured in units of  $a_0^2/a_0$ , with magnitudes equal to the matrix elements of  $\psi(r_1-r_2)^{-1}$  taken between basis states with  $a_0$  set to unity. Those with gradients are measured in units of  $a_0^2/a_0^2$ , the extra  $1/a_0$  being cancelled by a displacement  $\delta R$ .

Let us first of all consider those two-body matrix elements which contain just a single oxygen wavefunction. With the help of (8.3c), (8.6), (8.8), (8.9) and (8.12), we find the following expressions:

$$\begin{aligned} \langle 3sR, m_1 | U | m_2, m_3 \rangle &= C \, a_0^2/a_0, \\ C &= \frac{1}{4} \sum_{\lambda} \iint \psi(\lambda, r_1, R) \psi_{4f}(r_2) f(r, k) \psi_{4f}(r_1) \psi_{4f}(r_2) r_1^3 r_2^3 dr_1 dr_2 \\ &\quad \times \lambda(\lambda) \lambda(k) Y_{\lambda}^0(R) U(\lambda, R, k, Q, 3, m_2) U(3, R, k, Q, 3, m_3) \end{aligned} \quad (8.22)$$

A similar expression results when the off-site function is a  $2s$ -function, the only difference being in the radial integral. When the off-site function is a  $2p$ -function, the expression is more complicated:

$$\begin{aligned} \langle 2pRm_0, m_1 | U | m_2, m_3 \rangle &= 9.014 \, C \, a_0^2/a_0, \\ C &= \frac{1}{4} \sum_{\lambda} \iint r_1 a_0(0, r_1, R) \psi_{4f}(r_2) f(r, k) \psi_{4f}(r_1) \psi_{4f}(r_2) r_1^2 r_2^3 dr_1 dr_2 \end{aligned}$$

$$\begin{aligned}
& \times \lambda(1)\lambda(k)Y_0^0(R)U(3, \bar{m}_1, k, q, 3, m_3)V(1, \bar{m}, 1, \bar{m}_p, k, q, 3, m_2) \\
& - \frac{1}{4} \sum_{l, k} \iint R_{kl}(0, r_1, R) \nabla_{4f}(r_2) f(r, k) \nabla_{4f}(r_1) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\
& \times \lambda(1)\lambda(k)Y_0^0(R)Y_1^0(R)U(1, \bar{m}, k, q, 3, m_2)U(3, \bar{m}_1, k, q, 3, m_3) \quad (8.23)
\end{aligned}$$

In the first term of (8.23) we have defined a new function

$$V(a, e, b, f, c, g, d, h) = \int Y_a^e(\Omega) Y_b^f(\Omega) Y_c^g(\Omega) Y_d^h(\Omega) d\Omega \quad (8.24)$$

To evaluate (8.24) it is easiest to couple two of the spherical harmonics together to form a single harmonic [Edmonds 1959]. We then find that

$$\begin{aligned}
V(a, e, b, f, c, g, d, h) &= \sum_{lm} (4\pi)^{-4} [(2a+1)(2c+1)(2l+1)]^{-1/2} \\
&\times \begin{bmatrix} b & c & l \\ e & f & m \end{bmatrix} \begin{bmatrix} b & c & l \\ 0 & 0 & 0 \end{bmatrix} U(1, \bar{m}, e, c, d, h) \quad (8.25)
\end{aligned}$$

The other matrix elements involving  $U$  alone take the following forms:

$$\begin{aligned}
\langle 3pR, m_1 | U | 3pR', m_2 \rangle &= C \, a^2 / a_0, \\
C &= \frac{1}{4} \sum_{l, k} \sum_{lm} \iint \phi(L, r_1, R) \nabla_{4f}(r_2) f(r, k) \phi(1, r_1, R') \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \quad (8.26) \\
&\times \lambda(k)\lambda(1)\lambda(L) Y_L^0(R) Y_1^0(R') U(L, \bar{M}, k, q, 1, m) U(3, \bar{m}_1, k, q, 3, m_2) \\
\langle 2pR, m_1 | U | 3pR', m_2 \rangle &= 0.014 \, C \, a^2 / a_0, \\
C &= \frac{1}{4} \sum_{l, k} \sum_{lm} \iint r_1 a_L(0, r_1, R) \nabla_{4f}(r_2) f(r, k) \phi(1, r_2, R') \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\
&\times \lambda(k)\lambda(1)\lambda(L) Y_L^0(R) Y_1^0(R') V(L, \bar{M}, 1, \bar{m}_p, k, q, 1, m) U(3, \bar{m}_1, k, q, 3, m_2) \\
&- \frac{1}{4} \sum_{l, k} \sum_{lm} \iint R_{kl}(0, r_1, R) \nabla_{4f}(r_2) f(r, k) \phi(1, r_1, R') \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\
&\times \lambda(k)\lambda(1)\lambda(L) Y_L^0(R) Y_1^0(R') Y_1^0(R) U(L, \bar{M}, k, q, 1, m) U(3, \bar{m}_1, k, q, 3, m_2) \quad (8.27)
\end{aligned}$$

Similar expressions to (8.26) and (8.27) hold when one or more of the  $3p$ -functions are changed into  $2p$ -functions. Only the radial integrals change.

The calculation of two-body matrix elements with gradient operators in the integrand is a much more complicated problem, and the algebra becomes very severe when 2p-functions are involved. We will therefore estimate the value of any matrix element which contains a 2p-function and a second off-site function. As well as being rather complicated algebraically, these integrals are found to be difficult to obtain numerically, because the infinite series involved do not converge particularly quickly.

We obtain the following expressions for the matrix elements which are to be evaluated analytically. New quantities will be defined at the end of the section.

$$\langle m_1, m_2 | U \nabla_{1a} | 3a, m_3 \rangle = C \, a^2 / a_0^3,$$

$$\begin{aligned} C = & \sum_{Lk} \int \nabla_{4f}(r_1) \nabla_{4f}(r_2) f(r, k) G_1(L, r_1, R) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\ & \times \lambda(L) \lambda(k) Y_L^M(R) A(L, M, a) U(3, m_1, k, q, L+1, M+a) U(3, m_2, k, q, 3, m_3) \\ & - \sum_{Lk} \int \nabla_{4f}(r_1) \nabla_{4f}(r_2) f(r, k) G_2(L, r_1, R) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \quad (8.28) \\ & \times \lambda(L) \lambda(k) Y_L^M(R) B(L, M, a) U(3, m_1, k, q, L-1, M+a) U(3, m_2, k, q, 3, m_3) \end{aligned}$$

with a similar expression when the off-site function is a 2s-function.

$$\langle m_1, m_2 | U \nabla_{1a} | 2p, m_3 \rangle = 9.014 \, C \, a^2 / a_0^3,$$

$$\begin{aligned} C = & \sum_{Lk} A(1, -m, a) \int \nabla_{4f}(r_1) \nabla_{4f}(r_2) f(r, k) H_1(L, 1, r_1, R) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\ & \times \lambda(L) \lambda(k) Y_L^M(R) E(L, 1, M, m, m_p) U(3, m_1, k, q, 1+1, -m+a) U(3, m_2, k, q, 3, m_3) \\ & + \sum_{Lk} B(1, -m, a) \int \nabla_{4f}(r_1) \nabla_{4f}(r_2) f(r, k) H_2(L, 1, r_1, R) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\ & \times \lambda(L) \lambda(k) Y_L^M(R) E(L, 1, M, m, m_p) U(3, m_1, k, q, 1-1, -m+a) U(3, m_2, k, q, 3, m_3) \\ & - \sum_{Lk} A(L, M, a) \int \nabla_{4f}(r_1) \nabla_{4f}(r_2) f(r, k) H_3(L, r_1, R) \nabla_{4f}(r_2) r_1^2 r_2^2 dr_1 dr_2 \\ & \times \lambda(L) \lambda(k) Y_L^M(R) Y_1^M(R) U(3, m_1, k, q, L+1, M+a) U(3, m_2, k, q, 3, m_3) \end{aligned}$$



$$- \frac{1}{2} \sum_{L,k} B(L,M,a) \iint \Psi_{ef}(r_1) \Psi_{ef}(r_2) f(r,k) H_4(L,r_1,R) \Psi_{ef}(r_2) r_1^2 r_2^2 dr_1 dr_2 \times \lambda(L)\lambda(k) Y_L^M(R) Y_L^M(R) U(3,M_1,k,q,L-1,M+a) U(3,M_2,k,q,3,m_3) \quad (8.29)$$

$$\langle 3aR^1, m_1 | U \Psi_{1a} | 3aR, m_2 \rangle = C a^2 / a_1^2.$$

$$C = \frac{1}{2} \sum_{L,k} \sum_{M,m} A(L,M,a) \iint \phi(L,r_1,R') \Psi_{ef}(r_2) f(r,k) G_1(L,r_1,R) \Psi_{ef}(r_2) r_1^2 r_2^2 dr_1 dr_2 \times \lambda(L)\lambda(k)\lambda(k) Y_L^M(R') Y_L^M(R) U(L,M,k,q,L+1,M+a) U(3,M_1,k,q,3,m_2) - \frac{1}{2} \sum_{L,k} \sum_{M,m} B(L,M,a) \iint \phi(L,r_1,R') \Psi_{ef}(r_2) f(r,k) G_2(L,r_1,R) \Psi_{ef}(r_2) r_1^2 r_2^2 dr_1 dr_2 \times \lambda(L)\lambda(k)\lambda(k) Y_L^M(R') Y_L^M(R) U(L,M,k,q,L-1,M+a) U(3,M_1,k,q,3,m_2) \quad (8.30)$$

A similar expression to (8.30) holds when one or both of the 3s-functions become 2s-functions. In (8.28) to (8.30) we have defined the following new quantities:

$$G_1(L,r,R) = d/dr [\phi(L,r,R)] - L/r \phi(L,r,R) \quad (8.31a)$$

$$G_2(L,r,R) = d/dr [\phi(L,r,R)] + (L+1)/r \phi(L,r,R) \quad (8.31b)$$

$$H_1(L,l,r,R) = 9.014 (d/dr [ra_L(0,r,R)] - la_L(0,r,R)) \quad (8.32a)$$

$$H_2(L,l,r,R) = 9.014 (d/dr [ra_L(0,r,R)] + (l+1)a_L(0,r,R)) \quad (8.32b)$$

$$H_3(L,r,R) = 9.014R (d/dr [a_L(0,r,R)] - L/r a_L(0,r,R)) \quad (8.32c)$$

$$H_4(L,r,R) = 9.014R (d/dr [a_L(0,r,R)] + (L+1)/r a_L(0,r,R)) \quad (8.32d)$$

$$E(L,l,M,m,m_p) = (4\pi)^{-1} [5(2L+1)(2l+1)]^{1/2} \begin{bmatrix} 1 & 1 & 1 \\ m_p & M & m \end{bmatrix} \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{bmatrix} \quad (8.33)$$

Whenever a 2s-function appears in these matrix elements in place of a 3s-function, expressions (8.31a) and (8.31b) are replaced by

$$G_1(L,r,R) = 2.578 [d/dr (a_1(L,r,R)) - L/r a_1(L,r,R)] \quad (8.34a)$$

$$G_2(L,r,R) = 2.578 [d/dr (a_1(L,r,R)) + (L+1)/r a_1(L,r,R)] \quad (8.34b)$$

There is just one matrix element which we require now, namely

$$\langle m_1, 2pRm_p | U | m_2, 2pR'm_p \rangle$$

This matrix element is complicated to evaluate, and since it appears very infrequently in the terms in appendix A, we will provide an estimate of its value, as and when required.

## 8.6 Summary and Discussion

In this chapter we have concentrated on the techniques required to evaluate the matrix elements which appear in appendix A. We also discussed the choice of basis functions to be used, and in doing this we introduced some assumptions and approximations into the calculation. Perhaps the most notable of these is the way in which we choose the parameter  $A$  in the  $3s$ -orbital (8.4). We chose it so that the  $3s$ -orbital is orthogonal to the  $4f$ -functions, principally in an attempt to eliminate the need to use Lowdin's orthogonalization procedure, the result being a drastic reduction in the amount of computational work which needs to be done. The approximation certainly succeeds in this respect, but now we must ask if it is a "good" approximation; that is, can it be justified on physical grounds. The answer to this question is probably no. Since (8.4) is chosen to be an atomic orbital, it would seem reasonable to assume that its physical properties are going to be determined predominantly by the nature of the atom for which it is defined (i.e. the oxygen atom), and not by the properties of a crystal lattice in which the atom happens to be situated. This is the case for our choice of  $A$ . However there is one (accidental) mitigating feature. The choices for the coefficient  $A$  given in (8.7) are very close to those used by CEA in chapter three, and a glance at table 3.2 shows that small differences in the values of  $A$  [  $\Delta A = 0.2$  ] do not lead to pronounced changes in the order of magnitude or sign of the final result. Making a comparison in this way with the choice of CEA is of course only meaningful if it can be shown that their choice is a satisfactory one to begin with, a point to which we will return in the Conclusions chapter at the end of the thesis.

In the next chapter we will consider the numerical evaluation of these matrix elements, and by the end of this chapter we will be in a position to present our final estimate of the value of  $\mu_{\nu\bar{\nu}}$ .

## CHAPTER 9

### Numerical Evaluation of $\mu_{\text{eff}}$

#### 9.1 Introduction

In the previous chapter we derived expressions for all of the relevant matrix elements which appear in appendix A. Our problem now is to substitute the terms of appendix A into (6.19) and (6.20), and to tabulate  $A(j)$  and  $C(j)$  as functions of  $j$ . This is a problem of some complexity, and it requires the use of a computer. The reader will notice that most of the matrix elements in the previous chapter are written in a form which is particularly conducive to the use of a computer, in particular the fact that they are written as sums of products of functions which can easily be written as subroutines. Incidentally, it is worth comparing this approach with that used by CEA. Because the terms which appear in (3.22) are simpler than the ones which appear in our problem, they were able to perform the sums over the magnetic quantum numbers analytically (using the various orthogonality relations for  $3j$ -symbols), so that after evaluating the radial integrals the evaluation of  $\mu_{\text{eff}}$  was straightforward. The complexity of the terms in appendix A rules out this approach for our problem. In section 9.2 we will begin the presentation of our results. In order to use the computer program we need to know the radial integrals for the various matrix elements. In this section we will tabulate all of the radial integrals which are required for the two-body matrix elements, and we will provide complete expressions for the one-body matrix elements. We will also describe how we approximate those matrix elements which are not calculated analytically. In section 9.3 we will calculate the one quantity which we have not considered so far, namely the energy denominator  $\Delta$ . To evaluate  $\Delta$  we will use a many-electron approach in which we consider the energy difference between two Slater determinants, one for the configuration  $4f^7 5s^2 5p^6$ , and one for the configuration  $4f^8 5s^2 5p^6 : 3s$ , in which an electron is excited into a  $3s$ -state on a neighbouring oxygen atom. Finally, in section 9.4, we will present our final results, bringing together all of the intermediate results of chapter seven and this chapter.

## 9.2 Radial Integrals

In order to calculate the matrix elements which appear in the expression for  $\mu_{\text{ab}}$ , we need to know the radial integrals which appear in the various expressions in the previous chapter. In this section we will give complete expressions for the one-body matrix elements (except two-centre integrals belonging to categories e) f) g) and h) of (8.12), as these are too numerous to list in a convenient way, and we will list the radial integrals for the two-body matrix elements as functions of the appropriate ranks.

### 9.2a Categories a) b) c) and d)

The results quoted here are specifically for oxygen functions centred on an O(1) oxygen atom. To save space, the results for oxygen functions centred on an O(2) atom are obtained by substituting the numerical factors in the expressions for those in parentheses either at the end of the line or underneath the appropriate expression. Using the techniques outlined in section 8.4, we obtain the following results:

$$\langle 2sR | X | m \rangle = -0.0641 Y_2^m(R) e^2/a_0 \quad [-0.0422]$$

$$\langle 3sR | X | m \rangle = -0.0037 Y_2^m(R) e^2/a_0 \quad [-0.0017]$$

$$\begin{aligned} \langle 2pR m_p | X | m \rangle &= \{ (-1)^M (-0.9215) U(1, m_p, 2, -M, 3, m) Y_2^M(R) \\ &+ (-1)^M (-0.4846) U(1, m_p, 4, -M, 3, m) Y_4^M(R) \\ &- (-0.1075) Y_1^M(R) Y_3^M(R) \} e^2/a_0 \end{aligned}$$

O(2) atom: replace numerical factors with  $(-0.6546), (-0.3596), (-0.7118)$ .

$$\langle 2sR | V_a | m \rangle = [-0.0297 A(3, m, a) Y_4^m(R) - 0.0058 B(3, m, a) Y_2^m(R)] 1/a_0$$

O(2) atom: replace numerical factors with  $(-0.0209), (-0.0053)$

$$\langle 3sR | V_a | m \rangle = \{ 0.0350 A(3, m, a) Y_4^m(R) + 0.0131 B(3, m, a) Y_2^m(R) \} 1/a_0$$

O(2) atom: replace numerical factors with  $(0.0272), (0.0108)$

$$\begin{aligned}
\langle 2pRm_p | \nabla_a | m \rangle = & [(-1)^M(-0.4642) U(1, m_p, 3, -M, 4, m+a) A(3, m, a) Y_3^M(R) \\
& + (-1)^M(-0.2610) U(1, m_p, 5, -M, 4, m+a) A(3, m, a) Y_5^M(R) \\
& + (-1)^M(-0.2866) U(1, m_p, 1, -M, 2, m+a) B(3, m, a) Y_1^M(R) \\
& + (-1)^M(-0.0747) U(1, m_p, 3, -M, 2, m+a) B(3, m, a) Y_3^M(R) \\
& - (-0.0603) Y_1^M(R) Y_4^M(R) A(3, m, a) \\
& - (-0.6088) Y_1^M(R) Y_3^M(R) B(3, m, a)] 1/a_0
\end{aligned}$$

O(2) atom: replace numerical factors with  $(-0.3371), (-0.1989), (-0.2224)$   
 $(-0.0644), (-0.0464), (-0.3558)$

The matrix elements of  $XV_a$  and  $\nabla_a X$  have identical forms to the matrix elements of  $\nabla_a$ , except that they are measured in units of  $a^2/a_0$ . To avoid unnecessary duplication of the above expressions, we will simply give the numerical factors which should be substituted into the corresponding matrix element of  $\nabla_a$  given above.

$$\begin{aligned}
\langle 2sR | \nabla_a X | m \rangle : & \quad O(1) \text{ atom} \dots \quad (0.0306), (-0.2232) \\
& \quad O(2) \text{ atom} \dots \quad (0.0187), (-0.1366)
\end{aligned}$$

$$\begin{aligned}
\langle 3sR | \nabla_a X | m \rangle : & \quad O(1) \text{ atom} \dots \quad (-0.3971), (-0.4136) \\
& \quad O(2) \text{ atom} \dots \quad (-0.3006), (-0.3307)
\end{aligned}$$

$$\begin{aligned}
\langle 2pRm_p | \nabla_a X | m \rangle : & \quad O(1) \text{ atom} \dots \quad (0.4523), (0.2520), (1.2977) \\
& \quad \quad \quad \quad \quad \quad (0.1267), (0.5030), (-3.5318) \\
& \quad O(2) \text{ atom} \dots \quad (0.3329), (0.1987), (0.6859) \\
& \quad \quad \quad \quad \quad \quad (0.1070), (0.3591), (-2.2759)
\end{aligned}$$

$$\begin{aligned}
\langle 2sR | XV_a | m \rangle : & \quad O(1) \text{ atom} \dots \quad (0.0179), (0.2657) \\
& \quad O(2) \text{ atom} \dots \quad (0.0074), (0.1642)
\end{aligned}$$

$$\begin{aligned}
\langle 3sR | XV_a | m \rangle : & \quad O(1) \text{ atom} \dots \quad (-0.3385), (0.5694) \\
& \quad O(2) \text{ atom} \dots \quad (-0.2559), (0.4564)
\end{aligned}$$

$$\begin{aligned}
\langle 2pRm_p | XV_a | m \rangle : & \quad O(1) \text{ atom} \dots \quad (0.2566), (0.1543), (0.6244) \\
& \quad \quad \quad \quad \quad \quad (-0.0690), (0.2950), (-4.2179)
\end{aligned}$$

O(2) atom... (0.2019),(0.1283),(0.3885)  
 (-0.0240),(0.2153),(-2.7322)

## 9.2b Single Centre Integrals of Categories e) f) g) and h)

In general these integrals are easy to evaluate. The only minor difficulty arises in evaluating the last term of (8.17d), where it is necessary to expand  $|r-R|^{-1}$  using (8.8). Again the results quoted are for functions centred on an O(1) atom. The corresponding results for functions centred on an O(2) atom are given, where applicable, at the end of the line.

$$\langle 2sR | X | 2sR \rangle = -1.3674 \, a^2/a_0$$

$$\langle 2pR_{m_y} | X | 2pR_{m_y} \rangle = 0.3678 \, a^2/a_0$$

$$\langle 2sR | X | 3sR \rangle = -0.6019 \, a^2/a_0 \quad [-0.5335]$$

$$\langle 3sR | X | 3sR \rangle = -0.9746 \, a^2/a_0 \quad [-0.9578]$$

In the second matrix element above, a term corresponding to  $k=2$  in the expansion of  $|r-R|^{-1}$  has been ignored, as it is small by comparison with the leading terms in the expansion.

$$\langle 2pR_{m_y} | \nabla_x | 2sR \rangle = -1.1375 \, A(0,0,a) \, 1/a_0$$

$$\langle 2pR_{m_y} | \nabla_x | 3sR \rangle = 0.2996 \, A(0,0,a) \, 1/a_0 \quad [0.2125]$$

These matrix elements are only non-zero if  $m_y = a$ .

$$\langle 2pR_{m_y} | \nabla_x X | 3sR \rangle = A(0,0,a) [-3.1503 - 0.7039 \, Y_a(R)] \, a^2/a_0^2 \quad \dagger$$

O(2) atom: replace numerical factors with  $(-3.2035), (-0.6147)$

$$\langle 2pR_{m_y} | X \nabla_x | 3sR \rangle = A(0,0,a) [-3.1503 - 0.5834 \, Y_a(R)] \, a^2/a_0^2 \quad \dagger$$

O(2) atom: replace numerical factors with  $(-3.2035), (-0.5223)$

$$\begin{aligned}
\langle 2sR | X \nabla_a | 3sR \rangle &= A(0,0,a) [-0.5834] Y_1^0(R) a^2/a_0^3 & [-0.5223] \\
\langle 3sR | X \nabla_a | 2sR \rangle &= A(0,0,a) [0.4624] Y_1^0(R) a^2/a_0^3 & [0.4293] \\
\langle 3sR | X \nabla_a | 3sR \rangle &= A(0,0,a) [-0.6680] Y_1^0(R) a^2/a_0^3 & [-0.7701] \\
\langle 2sR | \nabla_a \nabla_b | 3sR \rangle &= A(0,0,a) B(1,b,a) [1.2038] 1/a_0^2 & [1.0670] \\
\langle 3sR | \nabla_a \nabla_b | 3sR \rangle &= A(0,0,a) B(1,b,a) [-2.3108] 1/a_0^2 & [-2.0045]
\end{aligned}$$

In the matrix elements marked with a dagger ( $\dagger$ ), we have again ignored a small term which originates from the  $k=2$  term in the expansion of  $1/r-R^{-1}$ . Note that the last seven matrix elements contain at least one  $3s$ -function; matrix elements such as  $\langle 2sR | X \nabla_a | 2sR \rangle$  do not appear in the calculation.

The list of one-body matrix elements is now complete. Two-centre integrals of categories e) f) g) and h) are calculated from within the computer program itself, because the huge diversity of integrals in these categories makes it inconvenient to tabulate them separately.

### 9.2c Two-Body Integrals With One Off-Site Function

In this section and the next we will tabulate the radial integrals for the two-body matrix elements given in section 8.5. In this section we will concentrate on those matrix elements which contain just a single off-site function, namely expressions (8.22), (8.23), (8.28) and (8.29). In dealing with those elements which contain more than one term (i.e. all of them except (8.22)), the first table of values will refer to the radial integral in the first term, the second table will refer to the radial integral in the second term, and so on and so forth. Note that all of the matrix elements in this section can be calculated exactly. Note also that because of the way the elements are constructed in section 8.5, these radial integrals are dimensionless numbers. The symbol  $R$  denotes the separation of the  $Gd^{3+}$  ion and the neighbouring oxygen atoms, in units of  $a_0$ .

$$\langle nsR, m_1 | U | m_2, m_2 \rangle \quad (\text{expression (8.22)})$$



Table 9.1a: radial integrals from (8.22)

| k | l | n=2 R=4.47 | n=3 R=4.47 | n=2 R=4.76 | n=3 R=4.76 |
|---|---|------------|------------|------------|------------|
| 0 | 3 | 0.0031     | 0.0008     | 0.0020     | 0.0006     |
| 2 | 1 | 0.0007     | 0.0080     | 0.00039    | 0.0070     |
| 2 | 3 | 0.0004     | 0.0004     | 0.0003     | 0.0003     |
| 2 | 5 | 0.0003     | 0.0002     | 0.0002     | 0.0002     |
| 4 | 1 | 0.0003     | 0.0045     | 0.0002     | 0.0040     |
| 4 | 3 | 0.0002     | 0.0002     | 0.0001     | 0.0002     |
| 4 | 5 | 0.00005    | -0.00004   | 0.00003    | -0.00004   |
| 4 | 7 | 0.00002    | -0.00002   | 0.00001    | -0.00002   |

 $\langle 2pR_{n,l} | U | 1m2, m3 \rangle$ 

(expression (8.23))

Table 9.1b: radial integrals from (8.23) (first term)

| k | l | R=4.4785 | R=4.7619 | k | l | R=4.4785 | R=4.7619 |
|---|---|----------|----------|---|---|----------|----------|
| 0 | 2 | 0.0021   | 0.0014   | 4 | 0 | 0.00002  | 0.00001  |
| 0 | 4 | 0.0025   | 0.0016   | 4 | 2 | 0.00005  | 0.00003  |
| 2 | 0 | 0.00007  | 0.00004  | 4 | 4 | 0.00004  | 0.00002  |
| 2 | 2 | 0.0002   | 0.0001   | 4 | 6 | 0.00002  | 0.00001  |
| 2 | 4 | 0.0002   | 0.0001   | 4 | 8 | 0.00001  | 0.00001  |
| 2 | 6 | 0.0001   | 0.0001   |   |   |          |          |

(continued on next page)

Table 9.1c: radial integrals from (8.23) (second term)

| k | i | R=4.4785 | R=4.7819 | k | i | R=4.4785 | R=4.7819 |
|---|---|----------|----------|---|---|----------|----------|
| 0 | 3 | 0.0034   | 0.0022   | 4 | 1 | 0.00016  | 0.00009  |
| 2 | 1 | 0.00038  | 0.00022  | 4 | 3 | 0.00010  | 0.00006  |
| 2 | 3 | 0.00035  | 0.00021  | 4 | 5 | 0.00005  | 0.00003  |
| 2 | 5 | 0.00023  | 0.00014  | 4 | 7 | 0.00003  | 0.00002  |

 $\langle m_1, m_2 | UV_{12} | n_1 R, m_3 \rangle$ 

(expression (8.28))

Table 9.1d: radial integrals from (8.28) (first term)

| k | i | n=2 R=4.47 | n=3 R=4.47 | n=2 R=4.78 | n=3 R=4.78 |
|---|---|------------|------------|------------|------------|
| 0 | 2 | 0.0011     | -0.0039    | 0.009      | -0.0030    |
| 2 | 0 | 0.0003     | 0.0004     | 0.0002     | 0.0003     |
| 2 | 2 | 0.0002     | -0.0008    | 0.0002     | -0.0006    |
| 2 | 4 | 0.00009    | -0.0002    | 0.00007    | -0.0001    |
| 4 | 0 | 0.0002     | 0.0003     | 0.0001     | 0.0002     |
| 4 | 2 | 0.0001     | -0.0003    | 0.00007    | -0.0002    |
| 4 | 4 | 0.00002    | -0.00005   | 0.00001    | -0.00003   |
| 4 | 6 | -0.000002  | 0.000007   | 0          | 0.000001   |

(continued on next page)

| Table 9.1e: radial integrals from (8.28) (second term) |   |            |            |            |            |  |
|--|---|------------|------------|------------|------------|--|
| k  | l | n=2 R=4.47 | n=3 R=4.47 | n=2 R=4.76 | n=3 R=4.76 |  |
| 0  | 4 | 0.0082     | -0.0054    | 0.0055     | -0.0041    |  |
| 2  | 2 | 0.0022     | 0.0111     | 0.0013     | 0.0090     |  |
| 2  | 4 | 0.0013     | -0.0006    | 0.0008     | -0.0004    |  |
| 2  | 6 | 0.0008     | -0.0003    | 0.0005     | -0.0002    |  |
| 4  | 2 | 0.0011     | 0.0085     | 0.0007     | 0.0053     |  |
| 4  | 4 | 0.0005     | -0.0002    | 0.0003     | -0.0001    |  |
| 4  | 6 | 0.0002     | -0.0002    | 0.0001     | -0.0002    |  |
| 4  | 8 | 0.00007    | -0.00008   | 0.00005    | -0.00007   |  |

$\langle m_1, m_2 | UV_{12} | 2pRm_0, m_3 \rangle$

(expression (8.29))

| Table 9.1f: radial integrals from (8.29) (first term) |   |   |          |          |   |   |   |          |          |
|---|---|---|----------|----------|---|---|---|----------|----------|
| k   | l | L | R=4.4785 | R=4.7619 | k | l | L | R=4.4785 | R=4.7619 |
| 0   | 2 | 1 | 0.0044   | 0.0024   | 4 | 0 | 1 | 0.0011   | 0.0006   |
| 0   | 2 | 3 | 0.0057   | 0.0030   | 4 | 2 | 1 | 0.0004   | 0.0002   |
| 2   | 0 | 1 | 0.0029   | 0.0015   | 4 | 2 | 3 | 0.0005   | 0.0003   |
| 2   | 2 | 1 | 0.0008   | 0.0005   | 4 | 4 | 3 | 0.0002   | 0.0001   |
| 2   | 2 | 3 | 0.0012   | 0.0006   | 4 | 4 | 5 | 0.0002   | 0.00008  |
| 2   | 4 | 3 | 0.0003   | 0.0002   | 4 | 6 | 5 | 0.0002   | 0.0001   |
| 2   | 4 | 5 | 0.0003   | 0.0002   | 4 | 6 | 7 | 0.00004  | 0.00002  |

(continued on the next page)

| Table 9.1g: radial integrals from (8.29) (second term) |   |   |          |          |   |   |   |          |          |
|--|---|---|----------|----------|---|---|---|----------|----------|
| k  | l | L | R=4.4785 | R=4.7619 | k | l | L | R=4.4785 | R=4.7619 |
| 0  | 4 | 3 | 0.0213   | 0.0111   | 4 | 2 | 1 | 0.0022   | 0.0012   |
| 0  | 4 | 5 | 0.0046   | 0.0024   | 4 | 2 | 3 | 0.0014   | 0.0007   |
| 2  | 2 | 1 | 0.0059   | 0.0031   | 4 | 4 | 3 | 0.0017   | 0.0009   |
| 2  | 2 | 3 | 0.0033   | 0.0017   | 4 | 4 | 5 | 0.0006   | 0.0003   |
| 2  | 4 | 3 | 0.0041   | 0.0021   | 4 | 6 | 5 | 0.0007   | 0.0004   |
| 2  | 4 | 5 | 0.0013   | 0.0007   | 4 | 6 | 7 | 0.0003   | 0.0001   |
| 2  | 6 | 5 | 0.0015   | 0.0008   | 4 | 8 | 7 | 0.0003   | 0.0001   |
| 2  | 6 | 7 | 0.0005   | 0.0003   | 4 | 8 | 9 | 0.0001   | 0.00005  |

| Table 9.1h: radial integrals from (8.29) (third term) |   |          |          |   |   |          |          |
|---|---|----------|----------|---|---|----------|----------|
| k   | L | R=4.4785 | R=4.7619 | k | L | R=4.4785 | R=4.7619 |
| 0   | 2 | 0.0106   | 0.0061   | 4 | 0 | 0.0010   | 0.0006   |
| 2   | 0 | 0.0027   | 0.0016   | 4 | 2 | 0.0008   | 0.0005   |
| 2   | 2 | 0.0020   | 0.0011   | 4 | 4 | 0.0002   | 0.0001   |
| 2   | 4 | 0.0005   | 0.0003   | 4 | 6 | 0.00005  | 0.00003  |

| Table 9.1j: radial integrals from (8.29) (fourth term) |   |          |          |   |   |          |          |
|--|---|----------|----------|---|---|----------|----------|
| k  | L | R=4.4785 | R=4.7619 | k | L | R=4.4785 | R=4.7619 |
| 0  | 4 | 0.0383   | 0.0209   | 4 | 2 | 0.0068   | 0.0038   |
| 2  | 2 | 0.0186   | 0.0104   | 4 | 4 | 0.0030   | 0.0017   |
| 2  | 4 | 0.0072   | 0.0040   | 4 | 6 | 0.0010   | 0.0005   |
| 2  | 6 | 0.0020   | 0.0011   | 4 | 8 | 0.0003   | 0.0002   |

#### 9.2d Two-Body Matrix Elements Containing Two Off-site Functions

In this section we will deal with those matrix elements which involve two off-site functions, namely expressions (8.26), (8.27) and (8.30), and any other matrix element whose value is to be estimated, rather than obtained

analytically. For this class of matrix elements we can no longer obtain exact expressions containing finite numbers of terms, as we could for the matrix elements in the previous section. Instead we must sum a set of infinite series - and hope that they converge fairly quickly. Fortunately, this procedure is quite easy to carry out in practice, for the dominant terms are found to arise from the  $k=0$  terms in the expansion of  $|r_1-r_2|^{-1}$ . The  $k=2$  terms are found to lead to radial integrals an order of magnitude or more smaller than those from the  $k=0$  terms, and this disparity is made even greater by an extra factor of  $1/5$  which comes from  $\lambda(k)$  in (8.8). We will therefore retain only the  $k=0$  terms in what follows.

`<nsR,m;UimsR'.ma>`

`(expression (8.26))`

| k | #  | L  | n=2 m=2<br>R=4.4785 | n=2 m=3<br>R=4.4785 | n=3 m=3<br>R=4.4785 | n=2 m=2<br>R=4.7619 | n=2 m=3<br>R=4.7619 | n=3 m=3<br>R=4.7619 |
|---|----|----|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 0 | 0  | 0  | 0.0010              | 0.0016              | 0.0047              | 0.0008              | 0.0013              | 0.0044              |
| 0 | 1  | 1  | 0.0080              | 0.0077              | 0.0146              | 0.0064              | 0.0066              | 0.0132              |
| 0 | 2  | 2  | 0.0164              | 0.0051              | 0.0079              | 0.0143              | 0.0040              | 0.0067              |
| 0 | 3  | 3  | 0.0225              | -0.0057             | 0.0058              | 0.0203              | -0.0059             | 0.0052              |
| 0 | 4  | 4  | 0.0239              | -0.0146             | 0.0112              | 0.0226              | -0.0141             | 0.0106              |
| 0 | 5  | 5  | 0.0214              | -0.0170             | 0.0145              | 0.0213              | -0.0165             | 0.0135              |
| 0 | 6  | 6  | 0.0169              | -0.0141             | 0.0127              | 0.0177              | -0.0139             | 0.0116              |
| 0 | 7  | 7  | 0.0121              | -0.0097             | 0.0084              | 0.0134              | -0.0095             | 0.0075              |
| 0 | 8  | 8  | 0.0081              | -0.0055             | 0.0045              | 0.0094              | -0.0054             | 0.0040              |
| 0 | 9  | 9  | 0.0050              | -0.0025             | 0.0021              | 0.0062              | -0.0024             | 0.0019              |
| 0 | 10 | 10 | 0.0029              | -0.0008             | 0.0012              | 0.0039              | -0.0007             | 0.0010              |
| 0 | 11 | 11 | 0.0011              | -0.0004             | 0.0006              | 0.0022              | -0.0005             | 0.0006              |

The cases when  $R \neq R'$  lead to similar sets of radial integrals. For the sake of brevity we will not include them here.

$\langle 2pR_{mp}, m; 1UlnaR, m_2 \rangle$

(expression (8.27))

| Table 9.11: radial integrals from (8.27) (first term) |    |    |              |              |              |              |
|---|----|----|--------------|--------------|--------------|--------------|
| k   | i  | L  | n=2 R=4.4785 | n=2 R=4.7619 | n=3 R=4.4785 | n=3 R=4.7619 |
| 0   | 0  | 1  | 0.0042       | 0.0037       | 0.0056       | 0.0051       |
| 0   | 1  | 0  | 0.0041       | 0.0036       | 0.0034       | 0.0031       |
| 0   | 1  | 2  | 0.0183       | 0.0165       | 0.0155       | 0.0141       |
| 0   | 2  | 1  | 0.0174       | 0.0158       | 0.0043       | 0.0034       |
| 0   | 2  | 3  | 0.0343       | 0.0317       | 0.0082       | 0.0067       |
| 0   | 3  | 2  | 0.0319       | 0.0298       | -0.0086      | -0.0089      |
| 0   | 3  | 4  | 0.0460       | 0.0439       | -0.0124      | -0.0131      |
| 0   | 4  | 3  | 0.0420       | 0.0405       | -0.0253      | -0.0247      |
| 0   | 4  | 5  | 0.0507       | 0.0501       | -0.0304      | -0.0303      |
| 0   | 5  | 4  | 0.0455       | 0.0454       | -0.0349      | -0.0336      |
| 0   | 5  | 6  | 0.0488       | 0.0501       | -0.0379      | -0.0367      |
| 0   | 6  | 5  | 0.0431       | 0.0447       | -0.0344      | -0.0330      |
| 0   | 6  | 7  | 0.0426       | 0.0454       | -0.0337      | -0.0331      |
| 0   | 7  | 6  | 0.0370       | 0.0401       | -0.0271      | -0.0258      |
| 0   | 7  | 8  | 0.0345       | 0.0383       | -0.0249      | -0.0243      |
| 0   | 8  | 7  | 0.0295       | 0.0333       | -0.0173      | -0.0162      |
| 0   | 8  | 9  | 0.0263       | 0.0305       | -0.0150      | -0.0144      |
| 0   | 9  | 8  | 0.0221       | 0.0261       | -0.0081      | -0.0072      |
| 0   | 9  | 10 | 0.0191       | 0.0231       | -0.0066      | -0.0059      |
| 0   | 10 | 9  | 0.0157       | 0.0195       | -0.0010      | -0.0008      |
| 0   | 10 | 11 | 0.0133       | 0.0168       | -0.0004      | -0.0003      |

(continued on the next page)

| Table 9.1m: radial integrals from (8.27) (second term) |    |    |              |              |              |              |
|--|----|----|--------------|--------------|--------------|--------------|
| k  | l  | L  | n=2 R=4.4785 | n=2 R=4.7619 | n=3 R=4.4785 | n=3 R=4.7619 |
| 0  | 0  | 0  | 0.0015       | 0.0013       | 0.0020       | 0.0018       |
| 0  | 1  | 1  | 0.0120       | 0.0107       | 0.0102       | 0.0097       |
| 0  | 2  | 2  | 0.0274       | 0.0251       | 0.0062       | 0.0050       |
| 0  | 3  | 3  | 0.0407       | 0.0364       | -0.0118      | -0.0121      |
| 0  | 4  | 4  | 0.0478       | 0.0487       | -0.0294      | -0.0289      |
| 0  | 5  | 5  | 0.0480       | 0.0486       | -0.0371      | -0.0361      |
| 0  | 6  | 6  | 0.0431       | 0.0455       | -0.0343      | -0.0333      |
| 0  | 7  | 7  | 0.0357       | 0.0393       | -0.0257      | -0.0248      |
| 0  | 8  | 8  | 0.0276       | 0.0317       | -0.0157      | -0.0149      |
| 0  | 9  | 9  | 0.0203       | 0.0243       | -0.0069      | -0.0061      |
| 0  | 10 | 10 | 0.0141       | 0.0168       | -0.0034      | -0.0038      |
| 0  | 11 | 11 | 0.0087       | 0.0095       | -0.0022      | -0.0025      |

Again, for the sake of brevity, we have not included the cases when  $R \neq R'$

$\langle n\mathbf{R}, m | U V_{12} | m\mathbf{R}', m_2 \rangle$  (expression (8.30))

| Table 9.1n: radial integrals from (8.30) (first term)<br>for the case $R = R' = 4.4785$ |    |   |         |         |         |         |
|---|----|---|---------|---------|---------|---------|
| k   | l  | L | n=2 m=2 | n=3 m=2 | n=2 m=3 | n=3 m=3 |
| 0   | 1  | 0 | -0.0016 | -0.0063 | -0.0051 | -0.0078 |
| 0   | 2  | 1 | -0.0041 | -0.0025 | -0.0041 | -0.0040 |
| 0   | 3  | 2 | -0.0116 | 0.0005  | 0.0008  | -0.0019 |
| 0   | 4  | 3 | -0.0191 | 0.0095  | 0.0091  | -0.0064 |
| 0   | 5  | 4 | -0.0243 | 0.0176  | 0.0179  | -0.0144 |
| 0   | 6  | 5 | -0.0238 | 0.0200  | 0.0206  | -0.0180 |
| 0   | 7  | 6 | -0.0209 | 0.0172  | 0.0179  | -0.0155 |
| 0   | 8  | 7 | -0.0165 | 0.0119  | 0.0125  | -0.0082 |
| 0   | 9  | 8 | -0.0119 | 0.0067  | 0.0072  | -0.0055 |
| 0   | 10 | 9 | -0.0080 | 0.0028  | 0.0031  | -0.0029 |

Table 9.1p: radial integrals from (8.36) (first term)  
for the case  $R = R' = 4.7619$

| k | L  | l | n=2 m=2  | n=3 m=2 | n=2 m=3 | n=3 m=3 |
|---|----|---|----------|---------|---------|---------|
| 0 | 1  | 0 | -0.0013  | -0.0055 | -0.0044 | -0.0059 |
| 0 | 2  | 1 | -0.0033  | -0.0020 | -0.0033 | -0.0030 |
| 0 | 3  | 2 | -0.0086  | 0.0070  | -0.0003 | -0.0012 |
| 0 | 4  | 3 | -0.0166  | 0.0086  | 0.0084  | -0.0055 |
| 0 | 5  | 4 | -0.0214  | 0.0158  | 0.0163  | -0.0128 |
| 0 | 6  | 5 | -0.02229 | 0.0182  | 0.0189  | -0.0157 |
| 0 | 7  | 6 | -0.0213  | 0.0158  | 0.0166  | -0.0132 |
| 0 | 8  | 7 | -0.0177  | 0.0110  | 0.0117  | -0.0049 |
| 0 | 9  | 8 | -0.0136  | 0.0061  | 0.0067  | -0.0046 |
| 0 | 10 | 9 | -0.0096  | 0.0023  | 0.0027  | -0.0024 |

Table 9.1q: radial integrals from (8.36) (second term)  
for the case  $R = R' = 4.765$

| k | L | l  | n=2 m=2 | n=3 m=2 | n=2 m=3 | n=3 m=3 |
|---|---|----|---------|---------|---------|---------|
| 0 | 0 | 1  | 0.0010  | 0.0021  | 0.0011  | 0.0046  |
| 0 | 1 | 2  | 0.0068  | 0.0069  | 0.0033  | 0.0069  |
| 0 | 2 | 3  | 0.0161  | 0.0021  | -0.0017 | 0.0031  |
| 0 | 3 | 4  | 0.0244  | -0.0105 | -0.0129 | 0.0083  |
| 0 | 4 | 5  | 0.0286  | -0.0211 | -0.0217 | 0.0176  |
| 0 | 5 | 6  | 0.0281  | -0.0240 | -0.0236 | 0.0212  |
| 0 | 6 | 7  | 0.0241  | -0.0206 | -0.0197 | 0.0178  |
| 0 | 7 | 8  | 0.0167  | -0.0143 | -0.0134 | 0.0115  |
| 0 | 8 | 9  | 0.0133  | -0.0081 | -0.0074 | 0.0061  |
| 0 | 9 | 10 | 0.0088  | -0.0035 | -0.0029 | 0.0032  |

(continued on the next page)



Table 2.1r radial integrals from (8.36) (second term)  
for the case  $R = R' = 4.7619$

| k | L | l  | n=2 m=2 | n=3 m=2 | n=2 m=3 | n=3 m=3 |
|---|---|----|---------|---------|---------|---------|
| 0 | 0 | 1  | 0.0008  | 0.0018  | 0.0008  | 0.0042  |
| 0 | 1 | 2  | 0.0054  | 0.0056  | 0.0026  | 0.0060  |
| 0 | 2 | 3  | 0.0133  | 0.0013  | -0.0018 | 0.0028  |
| 0 | 3 | 4  | 0.0212  | -0.0098 | -0.0116 | 0.0076  |
| 0 | 4 | 5  | 0.0261  | -0.0192 | -0.0195 | 0.0157  |
| 0 | 5 | 6  | 0.0270  | -0.0221 | -0.0214 | 0.0185  |
| 0 | 6 | 7  | 0.0245  | -0.0191 | -0.0181 | 0.0152  |
| 0 | 7 | 8  | 0.0201  | -0.0133 | -0.0123 | 0.0096  |
| 0 | 8 | 9  | 0.0151  | -0.0075 | -0.0067 | 0.0051  |
| 0 | 9 | 10 | 0.0107  | -0.0031 | -0.0025 | 0.0026  |

The reader may wonder why some of these tables of integrals have been truncated at a point where it would appear that the integrals have not converged. The reason is that the factors  $\lambda(L)\lambda(l)$ , which appear in the expressions for the matrix elements in chapter eight, force the actual terms in the matrix elements to converge faster than might at first appear to be the case.

As we have already mentioned, some of the matrix elements which appear in appendix A have been estimated. There are several reasons for this. Firstly some of them take algebraically complex forms, and so would require a lot of computational effort to evaluate. This effort would be justified if they appeared frequently in the calculation, but many of them do not. The ones to be estimated are  $\langle 2pRm_p, m_l | UV_1, 1 | 3sR', m_s \rangle$ ,  $\langle 3sR, m_l | UV_1, 1 | 2pR', m_p, m_s \rangle$  and  $\langle 2pRm_p, m_l | U | 2pR', m_p, m_s \rangle$ . To estimate the first and second of these elements we begin by noting that the radial part of the 2p-function is the same as that of the 2s-function (a consequence of the fact that they are both Slater orbitals). Therefore the extent of the overlap between the constituent wavefunctions will be similar to that for the case where a 2s-function replaces the 2p-function in the matrix elements. We will therefore approximate these matrix elements as follows:

$$\langle 2pRm_p, m_1 | U\bar{V}_{1a} | 3aR', m_2 \rangle = \langle 2aR, m_1 | U\bar{V}_{1a} | 3aR', m_2 \rangle$$

$$\langle 3aR, m_1 | U\bar{V}_{1a} | 2pR', m_p, m_2 \rangle = \langle 3aR, m_1 | U\bar{V}_{1a} | 2aR, m_2 \rangle$$

The third matrix element appears only three times in the whole calculation and will be approximated as follows:

$$\begin{aligned} \langle 2pRm_p, m_1 | U | 2pR', m_p, m_2 \rangle &= e^2/2R \quad \text{if } m_1 = m_2, m_p = m_p, R=R' \\ &= \langle 2aR, m_1 | U | 2aR', m_2 \rangle \quad \text{otherwise.} \end{aligned}$$

This now completes the tabulation of the matrix elements required to find  $\mu_{ab}$ . We require just one quantity now, namely  $\Delta$ .

### 9.3 The Energy Denominator $\Delta$

The energy denominator  $\Delta$  appears as part of the second order correction to the effective operator  $H_{eff}$ , and is equal to the energy difference between the excited and ground families of states appropriate to our calculation. That is, it is equal to the energy difference between the family of states in which the  $Gd^{3+}$  ion is in its  $^8S_{7/2}$  ground state (for simplicity we will ignore the effects of intermediate coupling), and the family in which one of the 4f-electrons has been excited into an empty 3s-orbital on a neighbouring oxygen atom.

Let us then consider a system consisting of a gadolinium nucleus, into which is absorbed the  $1s^2 2s^2 \dots 4d^{10}$  core electrons, giving an effective nuclear charge of +18 (64-46). The 4f, 5s and 5p-electrons move in the electric field of this charge. At a position vector  $R$  away is situated an oxygen atom, which, following CEA, we will assume to have an effective charge of +1. The Hamiltonian for this system is then

$$H = \sum_i (p_i^2/2m_i) - \sum_i 18e^2/r_i - \sum_i e^2/|r_i - R| + \sum_{j \in O} e^2/r_{ij} \quad (9.1)$$

It is straightforward to write down a many-electron state which belongs to the ground family. The state

$$|\Phi_2\rangle = \{\varphi_{4f}(1)\varphi_{4f}(2)\varphi_{4f}(3)\varphi_{4f}(4)\varphi_{4f}(5)\varphi_{4f}(6)\varphi_{4f}(7)\varphi_{3d}(1)\varphi_{3d}(2) \\ \theta_{5p}(1)\theta_{5p}(2)\theta_{5p}(3)\theta_{5p}(4)\theta_{5p}(5)\theta_{5p}(6)\} \quad (9.2)$$

describes a state which, in LS-coupling, has  $L=0, S=7/2, J=7/2$  and  $M_J=7/2$ , if we insist that all seven 4f-electrons are in their  $m_s = +\frac{1}{2}$  spin states. The states with different values of  $M_J$  are degenerate with this state. The Slater determinant

$$|\Phi_3\rangle = \{\varphi_{4f}(1)\varphi_{4f}(2)\varphi_{4f}(3)\varphi_{4f}(4)\varphi_{4f}(5)\varphi_{4f}(6)\Psi_{3d}(1)\varphi_{3d}(2) \\ \theta_{5p}(1)\theta_{5p}(2)\theta_{5p}(3)\theta_{5p}(4)\theta_{5p}(5)\theta_{5p}(6)\} \quad (9.3)$$

describes an excited state in which one of the 4f-electrons has been excited into an empty 3d-orbital on an oxygen neighbour.  $\Delta$  is then given by

$$\Delta = \langle \Phi_2 | H | \Phi_2 \rangle - \langle \Phi_3 | H | \Phi_3 \rangle \quad (9.4)$$

The rules for obtaining the matrix elements of Slater determinants are well known [Zeiger and Prent 1973]. Applying them to this expression gives

$$\Delta = \langle \Psi_{3d}(1) | h_1 | \Psi_{3d}(1) \rangle - \langle \varphi_{4f}(7) | h_1 | \varphi_{4f}(7) \rangle \\ + \sum_{m=1}^6 \{ \langle \varphi_{4f}(m), \Psi_{3d}(1) | h_2 | \varphi_{4f}(m), \Psi_{3d}(1) \rangle \\ + \langle \varphi_{4f}(m), \varphi_{4f}(7) | h_2 | \varphi_{4f}(7), \varphi_{4f}(m) \rangle \\ - \langle \varphi_{4f}(m), \Psi_{3d}(1) | h_2 | \Psi_{3d}(1), \varphi_{4f}(m) \rangle \\ - \langle \varphi_{4f}(m), \varphi_{4f}(7) | h_2 | \varphi_{4f}(m), \varphi_{4f}(7) \rangle \\ + \langle \theta_{5p}(m), \Psi_{3d}(1) | h_2 | \theta_{5p}(m), \Psi_{3d}(1) \rangle \\ + \langle \theta_{5p}(m), \varphi_{4f}(7) | h_2 | \varphi_{4f}(7), \theta_{5p}(m) \rangle \\ - \langle \theta_{5p}(m), \varphi_{4f}(7) | h_2 | \theta_{5p}(m), \varphi_{4f}(7) \rangle \\ - \langle \theta_{5p}(m), \Psi_{3d}(1) | h_2 | \Psi_{3d}(1), \theta_{5p}(m) \rangle \} \\ + \sum_{m=1}^6 \{ \langle \theta_{5d}(m), \Psi_{3d}(1) | h_2 | \theta_{5d}(m), \Psi_{3d}(1) \rangle \\ + \langle \theta_{5d}(m), \varphi_{4f}(7) | h_2 | \varphi_{4f}(7), \theta_{5d}(m) \rangle \\ - \langle \theta_{5d}(m), \varphi_{4f}(7) | h_2 | \theta_{5d}(m), \varphi_{4f}(7) \rangle \\ - \langle \theta_{5d}(m), \Psi_{3d}(1) | h_2 | \Psi_{3d}(1), \theta_{5d}(m) \rangle \} \quad (9.5)$$

In this expression we have defined the following new quantities:

$$h_1 = p^2/2m - 18e^2/r - e^2/|r-R|$$

$$h_2 = e^2/|r_1-r_2|$$

To evaluate  $\Delta$  we will take the 4f-functions to be those of Freeman and Watson (1962), and the 3s-oxygen wavefunction to be that given by (8.4), with the parameter  $A$  given in (8.7). For the 5s and 5p-functions we will use Slater orbitals [Griffiths 1962]. The 5s and 5p-functions then have the same radial dependence, which is found to be

$$17.70/a_0^3 r^3 \exp(-3.075r/a_0) \quad (9.6)$$

We can now evaluate (9.5), with the help of the techniques described in the previous chapter. We must however be careful to remember that spin orthogonality will ensure that some of the terms in (9.5) are automatically zero. To check the likely accuracy of the final result, suppose that the 3s-orbital is situated at infinity. We then find that  $\Delta = +1.87$  atomic units. Physically this must correspond to the energy required to remove a 4f-electron from the  $Gd^{3+}$  ion, and indeed we find that this value is in good agreement with the experimental value of 1.63 atomic units [Sugar and Reader 1976]. Note that this result is found to be independent of the magnetic quantum number of the 4f-electron which is removed.

In evaluating the full expression (9.5), we will ignore the fact that  $\Delta$  will be different for excitations to  $O(1)$  and  $O(2)$  atoms. Instead we will obtain a mean value (which is in fact what the Method of Stevens requires us to use). The value we obtain is

$$\Delta = 1.644 \text{ atomic units} = 3.6 \times 10^5 \text{ cm}^{-1} \quad (9.7)$$

Errors in this value are likely to arise from the imprecise forms chosen for the 5s and 5p-functions, plus the fact that they are not necessarily orthogonal to the 3s-functions on the oxygen neighbours.

#### 9.4. Final Results

We are now finally in a position to obtain the contribution which our mechanism makes to the SCCF, using the results of chapter seven, chapter eight and this chapter. What we need to do is to tabulate the coefficients  $A(j)$  and  $C(j)$  in (6.19) and (6.20) as functions of the normal coordinate labels  $j$ . For convenience we will retain the numbering scheme of appendix A, so that  $A(j)$  is obtained by evaluating terms (1) to (42) in (6.19), and  $C(j)$  is obtained by evaluating terms (43) to (105) in (6.20). The contributions of each individual term to  $A(j)$  and  $C(j)$  are given in appendix E.

Now, using the results for the normal coordinate frequencies  $\omega_j$  given in chapter seven, we can combine (6.17) and (6.18) and the results of appendix E to arrive at a closed expression for  $\mu_{\nu b}$ . However we must be careful with units again. The coefficients  $A(j)$  and  $C(j)$  are measured in units of  $(e^2/\epsilon_0)^{1/2} \cdot 1/a_0^3$ , the first factor arising from the operators  $X$  and  $U$ , the second from the gradient operators. Bearing all of this in mind, along with the value (9.7) for  $\Delta$  and the fact that  $N_1^2=7$ ,  $N_2^2=189$  for  $f$ -electrons, we find that  $\mu_{\nu b}$  is given by

$$\begin{aligned} \mu_{\nu b} &= \mu_1 + \mu_2 + \mu_3 + \mu_4 \\ &= -1.142 \times 10^{16}/\mu \{ 0.00040 \coth(1.16 \times 10^{-12}\omega/T) \\ &\quad + 0.00033 \coth(1.22 \times 10^{-12}\omega/T) \\ &\quad + 0.0117 \coth(3.85 \times 10^{-12}\omega/T) \\ &\quad - 0.0103 \coth(4.03 \times 10^{-12}\omega/T) \} \text{ cm}^{-1}. \end{aligned}$$

The characteristic frequency  $\omega$  was determined in chapter seven by matching the results obtained with the Restricted model of lattice vibrations with those obtained from the Debye/Einstein models.

To convert the contribution  $\mu_{\nu b}$  into an actual zero field splitting, it is best to use arguments similar to those given in section 3.7. In that section it was concluded that a contribution of  $\mu=148.3 \text{ cm}^{-1}$  to the SCCF coefficient led to a contribution of  $+0.853 \text{ cm}^{-1}$  to the actual zero field

splitting (this proportionality can be found by evaluating the matrix elements of the SCCF between the  $M_J = \pm 7/2$  and  $M_J = \pm 1/2$  states of the  $|^8S_{7/2}\rangle$  ground state). Therefore to convert  $\mu_{\nu b}$  to an actual zero field splitting, all we need do is multiply it by 0.853/148.3. The final results are shown in table 9.2.

| T/K | $\omega = 1.70 \times 10^{13} \text{ s}^{-1}$<br>( $\theta_D = 65\text{K}$ ) |          | $\omega = 4.04 \times 10^{13} \text{ s}^{-1}$<br>( $\theta_D = 125\text{K}$ ) |          | $\omega = 4.35 \times 10^{13} \text{ s}^{-1}$<br>( $\theta_D = 167\text{K}$ ) |          |
|-----|--|----------|---|----------|---|----------|
|     | $\mu_{\nu b}$  | ZFS      | $\mu_{\nu b}$   | ZFS      | $\mu_{\nu b}$   | ZFS      |
| 10  | - 1.0779   | - 0.0062 | - 0.3901  | - 0.0022 | - 0.3613  | - 0.0021 |
| 30  | - 2.2615   | - 0.0130 | - 0.5020  | - 0.0029 | - 0.4498  | - 0.0026 |
| 50  | - 3.6580   | - 0.0210 | - 0.7031  | - 0.0040 | - 0.6166  | - 0.0036 |
| 70  | - 5.0825   | - 0.0292 | - 0.9361  | - 0.0054 | - 0.8140  | - 0.0047 |
| 90  | - 6.5149   | - 0.0375 | - 1.1801  | - 0.0068 | - 1.0227  | - 0.0059 |
| 110 | - 7.9507   | - 0.0457 | - 1.4288  | - 0.0082 | - 1.2361  | - 0.0071 |
| 130 | - 9.3883   | - 0.0540 | - 1.6797  | - 0.0097 | - 1.4518  | - 0.0084 |
| 150 | - 10.8269  | - 0.0623 | - 1.9319  | - 0.0111 | - 1.6689  | - 0.0096 |
| 170 | - 12.2662  | - 0.0706 | - 2.1848  | - 0.0126 | - 1.8868  | - 0.0109 |
| 190 | - 13.7058  | - 0.0783 | - 2.4383  | - 0.0140 | - 2.1051  | - 0.0121 |
| 210 | - 15.1458  | - 0.0871 | - 2.6921  | - 0.0155 | - 2.3239  | - 0.0134 |
| 230 | - 16.5861  | - 0.0954 | - 2.9462  | - 0.0170 | - 2.5428  | - 0.0146 |
| 250 | - 18.0265  | - 0.1037 | - 3.2005  | - 0.0184 | - 2.7620  | - 0.0159 |
| 270 | - 19.4670  | - 0.1120 | - 3.4549  | - 0.0199 | - 2.9813  | - 0.0172 |
| 290 | - 22.3483  | - 0.1203 | - 3.7094  | - 0.0213 | - 3.2008  | - 0.0184 |

In view of the comments that were made at the start of chapter four, it would seem that our mechanism leads to a contribution of the right order of magnitude and sign to produce good agreement with the experimental zero field splitting of  $\Delta E = +0.236 \text{ cm}^{-1}$ . We will discuss the full implications of these results in the Conclusions chapter which follows.

## CONCLUSIONS

Table 9.2 contains the final results of our calculation. There we present the contribution  $\mu_{\text{eff}}$  of our mechanism, along with the corresponding zero field splitting, as a function of the temperature of the lattice, and as a function of the three different values of the Debye temperature (and hence  $\omega$ ) which we introduced in chapter seven. In trying to interpret these results, there are two fundamental questions which we should ask ourselves. Firstly, in view of the number of approximations and assumptions which we have made throughout the course of this thesis, can we trust the results to be a reasonably accurate estimate of the true state of affairs? Then, if we can trust the results, are they sufficient to provide an adequate explanation of the experimental data, when they are added to the existing mechanisms given in chapters one, two and three? In this concluding section we will attempt to answer both of these questions.

Mechanisms of the type discussed in chapter three and the main body of this thesis are often referred to as "inter-site" mechanisms, the prefix "inter" denoting the fact that an electron is excited into an orbital on a neighbouring ligand, rather than an excited state on the  $\text{Gd}^{3+}$  ion (on-site mechanism). Since the  $4f$ -functions are known accurately, one would expect that the greatest errors in the numerical part of the calculation will be incurred as a result of uncertainties in the choice of wavefunction for the excited orbital. Let us then discuss in more detail the choice of off-site wavefunctions. Because our calculation is essentially qualitative in nature, one would like to choose states which lead to as simple a formalism as possible. Therefore it is assumed that electrons are excited into empty  $3s$ -states on the neighbouring oxygen atoms. Strictly speaking, we should consider molecular orbitals appropriate to a water molecule, but this would introduce undesirable complications into the formalism. To the best of our knowledge, an accurate wavefunction for such a  $3s$ -state is not available. Therefore an approximation must be found, again bearing in mind our objective of keeping things as simple as possible. To this end, the  $3s$ -state is chosen to be of hydrogenic form, with a single free parameter  $A$ . In this thesis,  $A$  is chosen so as to make the  $3s$ -orbital orthogonal to the  $4f$ -states on the  $\text{Gd}^{3+}$  ion. The main reason for doing this is to effect

an enormous simplification into the algebra involved in the problem. The 3s-orbital is then orthogonalized to the other functions on the same site using Lowdin's orthogonalization procedure. To see why this procedure leads to a simplification, suppose that the 3s and 4f-orbitals are not orthogonal, so that the procedure of Lowdin must be used. From (3.26a) and (3.26b) we see that the matrix elements of the new orthogonalized orbitals will involve on-site matrix elements of the form  $\langle m_1 | X | m_1 \rangle$ ,  $\langle m_1, m_2 | U | m_1, m_2 \rangle$  etc., multiplied by overlaps of the form  $\langle m_1 | 3sR \rangle$ . These on-site matrix elements are very large; for instance  $\langle m_1 | X | m_1 \rangle = 7a^2/a_0$ . Thus, unless the overlaps  $\langle m_1 | 3sR \rangle$  are very small, the corrections introduced by the orthogonalization procedure are unlikely to be small. CEA (chapter three) followed this procedure, because they chose A so as to minimise the sum of the squares of the overlaps of the 3s-function with the 1s and 2s-functions on the same site. In view of the relative simplicity of their calculation (compared with the work of this thesis), this procedure is not an unreasonable one to follow. However a glance at appendix A shows that for our problem the procedure would lead to a horrendous numerical problem, which would take a considerable amount of time to solve. The terms in appendix A are complicated enough even before any corrections for non-orthogonality are introduced! We therefore chose A so as to eliminate this problem at the outset. If the 3s-function is then orthogonalized to the 1s and 2s-functions on the same site using Lowdin's procedure, one can easily show that the corrections introduced into the matrix elements are much smaller (see section 8.2), and as such can safely be ignored.

We have already argued at the end of chapter eight that our choice of A does not really have a sound physical basis. However we should point out that A is not defined uniquely by minimising the sum of the squares of the overlaps of the 3s-functions with the 1s and 2s-functions. CEA used a value of  $A = 1.67a_0^2$ , but a second choice based on this minimization procedure could be  $A = 0.42a_0^2$  (which in fact leads to an orbital which is "more orthogonal" than the one with  $A = 1.67a_0^2$ ). In view of the intrinsic uncertainty in the form of the 3s-orbital to begin with, it is debatable as to which would be the best choice of A. The corollary of this is that it is arguable as to whether the choice of CEA is any better than the one



used in this thesis. What is required of course is a more careful examination of the nature of an excited  $3s$ -state for oxygen.

Most of the other approximations made are less "controversial" than the choice of  $3s$ -orbital, since they involve the neglect of terms in the Hamiltonian or from appendix A which are small, and are therefore unlikely to influence the final result to any great extent. For instance, we can safely drop the crystal field terms from the Hamiltonian (5.1), because they will be small compared with the attraction which the electrons feel from the  $Gd^{3+}$  ion. Similarly we can drop terms from appendix A which contain two-body exchange-like matrix elements, because these are easily demonstrated to be small. For the same reasons we can drop the  $1s$ -functions from the basis set in chapter eight.

It is likely that the Method of Stevens is the best way of calculating spin correlated crystal field operators, because the method is very careful to ensure that all of the appropriate symmetries are incorporated into the effective Hamiltonian  $H_{eff}$  (to all orders in the perturbation expansion). In addition, the very careful definition of the unperturbed Hamiltonian means that one is unlikely to run into technical problems of the sort which can arise when one is performing perturbation theory on an infinite system (e.g. overlapping of energy levels from different manifolds). In modifying the Method of Stevens for use in a dynamic lattice, our aim was to try and retain all of these features, whilst at the same time retaining the simplicity of the formalism for the static lattice. The result (chapter four) is a new effective operator which is very similar in form to that for the static lattice, and which is identical to that given by Sigmund and Stevens (1988) in an earlier paper. Towards the end of chapter four we attempted to point out that more exact approaches to the problem could lead to pitfalls whose consequences would be hard to predict.

Our choice for the model of lattice vibrations (chapters six and seven) was dictated largely by the fact that there is a distinct lack of appropriate experimental data in the literature. In such circumstances the author believes that as simple a model as possible should be used, with as

few adjustable parameters as possible. Fortunately such a procedure is made easier in the case considered in this thesis if we consider just the normal coordinates of the nearest neighbours of the  $Gd^{3+}$  ion. We then have just two types of force constant to consider, and if we write one as a multiple of the other ( $k_1 = \lambda k_2$  with  $\lambda$  known reasonably well), we are left with just one adjustable parameter to choose. In chapter seven we did this by matching up data from our "Restricted model" with data which could be obtained from a knowledge of the Debye temperature(s) of GdES. The normal coordinates in the Restricted model are obtained by standard means.

For the 1s 2s and 2p-orbitals in chapters eight and nine we chose to use Slater orbitals, principally on account of their simplicity and ease of use. Although Slater orbitals are nodeless functions (in contrast to the true atomic wavefunctions), it is known that they provide a reasonable approximation to the true wavefunctions for large values of  $r$ . Since it is in this region that the overlap with the 4f-functions is greatest, one would expect that integrals of the form  $\langle m|O|2sR \rangle$  etc. will be obtained relatively accurately. On the other hand, integrals such as  $\langle 2sR|O|2sR \rangle$  may not. In retrospect it may have been better to use the accurate radial functions of Clementi and Roetti (1974), but given our comments earlier about the 3s-functions, it would be difficult to know whether the new set of results would be any more accurate.

In conclusion then, it is unlikely that we can trust the results in table 9.2 to be exact values, but we would consider it unlikely that the approximations are sufficient to seriously affect the order of magnitude or sign of these results. Therefore we will consider the interpretation of these results on the understanding that the sign and order of magnitude are correct (i.e. ZFS = -0.1 to -0.01  $cm^{-1}$ ). We still, of course, have the problem of deciding which value of the characteristic frequency  $\omega$  to choose (remember  $\omega^2 = k/M$ , where  $k$  is the Gd-O stretching force constant). It has been suggested (Pettifer, private communication) that a value of  $\hbar\omega = 200\text{ }cm^{-1}$  is likely to be of the correct order of magnitude. This gives  $\omega = 3.7 \times 10^{13}\text{ }s^{-1}$ , and suggests that the final four columns of table 9.2 are where we should focus our attention. It is also interesting to note that the values of  $\theta_0$  which lead to the corresponding values of  $\omega$  (155K

and 167K) were obtained with the help of approximations very similar to those which were made in chapters six and seven. For instance,  $\theta_D = 155K$  [Pepoulat 1962] is obtained by matching up specific heat data with a combined Debye/Einstein model, and  $\theta_D = 167K$  [McColl 1968] is calculated on the assumption that the motion of the ethylsulphate radicals and the internal motion of the water molecules can be ignored. The results of table 9.2 would seem to indicate that the sign and order of magnitude of the final results does not depend crucially on the exact value of  $\theta_D$  for  $\theta_D = 150K$ . The value of  $\theta_D = 85K$  is obtained by matching the Debye model with spin-lattice relaxation data [Krygin et al 1981].

In order to determine whether the results are "correct" or not, we need to add them to the results of chapters one, two and three, and compare them with the experimental data of table 4.1. As we mentioned right at the start of chapter four, the inter-site mechanism of chapter three poses similar problems to our mechanism, in the sense that we have to make a decision as to which is the best value to take from table 3.2. This has been done [Tuszynski and Dixon 1987], and the value of the zero field splitting when all of the mechanisms up to the end of chapter three are added together is

$$\Delta E = + 0.279 \text{ cm}^{-1}$$

If we examine table 4.1, then we see that this value is higher than the experimental splittings. Therefore any new mechanisms need to be negative in order to improve agreement with experiment. Our mechanism certainly succeeds in this respect. If we look at the entry for  $T = 285K$  in table 4.1, then we see that new mechanisms must contribute  $\Delta E_z = -0.043 \text{ cm}^{-1}$  to the zero field splitting. From table 9.2 we see that our mechanism contributes about half of this value.

Now let us compare the actual temperature dependence of the zero field splitting with that which is predicted in table 9.2. According to table 4.1, the zero-field splitting initially increases with temperature, but then it reaches a maximum at around  $T = 130K$  and then decreases as temperature increases further. But the contribution from our mechanism is small

for low values of  $T$ , and becomes gradually more negative as temperature is increased, and when added to  $\Delta E$  above it predicts a zero field splitting which decreases monotonically with temperature. Therefore our mechanism does not predict the correct temperature dependence for the zero field splitting in the low temperature limit, and we must examine the reasons why it does not.

Firstly, we must remember that the inter-site mechanism of CEA is not the only one which is likely to change when the lattice is made to vibrate. All of the mechanisms described in chapters one and two were calculated on the assumption that the lattice is stationary, and one would be very surprised if a temperature dependent contribution did not arise from these mechanisms when the lattice is made to vibrate.

Secondly, most calculations to investigate the temperature dependence of zero field splittings or spin Hamiltonian parameters do not take the same approach as we have in this thesis. Instead they study the influence of the orbit-lattice interaction on these temperature dependencies. Because of the approximations made in connection with equation (5.8), the orbit-lattice interaction is in fact completely neglected in our calculation. This was done on account of the fact that it is likely to be small by comparison with other terms in the Hamiltonian (5.1). Nevertheless, some authors (for references see section 4.2) have concluded that the orbit-lattice interaction can be important, and so perhaps it should have been included in the calculation of  $\mu_{\text{eff}}$ . It is however a moot point as to whether incorporating it within the framework of this thesis leads to a more convenient formalism than that of other authors, who used the Van-Vleck (or spin-phonon) interactions.

Finally, since these temperature dependencies arise from the thermal averaging of the normal coordinates, it might be argued that the Restricted model of lattice vibrations is responsible for the discrepancy, in particular the fact that we have restricted ourselves to the harmonic approximation. It has been suggested [Dieke 1968] that the simplest explanation for the temperature dependence of the zero field splitting is that as the temperature increases, the lattice expands, and so the crystal

field parameters change. Such a mechanism cannot be present in the formalism of this thesis, because we have restricted ourselves to the harmonic approximation for the lattice vibrations, and to incorporate it would require us to include higher anharmonic terms from the expansion of the factors  $\exp(i\theta)$  which appear in (5.16). The reader will surely appreciate that to do such a calculation would be an extremely arduous task; what we can do, however, is consider the effects of thermal expansion by recalculating the mechanism of CEA (chapter three) as a function of the  $Gd^{3+}-O$  separation, and then relate this to the temperature of the lattice via the thermal expansion coefficient. The result is (for want of a better term) a 'static anharmonic mechanism'. Unfortunately, data concerning the thermal expansion coefficient  $\alpha$  for GdES does not appear to be available, but there is an expression for  $\alpha$ , due to Wilson and Bastow (1971), given by

$$\alpha = \frac{3\gamma}{a_0} \frac{1}{M} \left( \frac{h}{k_B \theta_D} \right)^2$$

where  $\gamma$  is known as the Gruneisen parameter,  $a_0$  is the separation between ligands and  $M$  is the mass of the ligands. Strictly speaking,  $\alpha$  should be temperature dependent, but for simplicity we will ignore this difficulty. Unfortunately  $\gamma$  is not known for GdES, but tables of data (e.g. that given in chapter 5 of Reissland (1972)) seem to indicate that  $\gamma$  varies between about 1 and 5. For simplicity we will take  $\gamma=3$ . By taking  $\theta_D=155K$ , we find that  $\alpha = 6 \times 10^{-5} K^{-1}$ . According to Gharbin and Reppart (1984), the Gd-O lengths quoted in chapter seven were measured at 171K. The bond lengths as a function of temperature are then

$$\begin{aligned} O(1) \text{ atom: } R_1 &= 4.4785[1+6 \times 10^{-5}(T-171)] \\ O(2) \text{ atom: } R_2 &= 4.7810[1+6 \times 10^{-5}(T-171)] \end{aligned}$$

With the help of these expressions, we have recalculated the contribution which the inter-site mechanism of CEA makes to the zero field splitting, as a function of the temperature of the lattice. For simplicity, we used the formalism of chapter three, but with the 3s-function chosen according to section 8.2. The results are summarised in the following table:

| $\mu_{eff}$ as a function of the temperature of the lattice (in $\text{cm}^{-1}$ ) |           |           |           |           |                                  |                                  |
|--|-----------|-----------|-----------|-----------|----------------------------------|----------------------------------|
| T/K  | $R_1/a_0$ | $A_1/a_0$ | $R_2/a_0$ | $A_2/a_0$ | $\mu_{eff}$ with $Z_{eff} = 3.0$ | $\mu_{eff}$ with $Z_{eff} = 3.5$ |
| 27.7   | 4.440     | 1.5361    | 4.721     | 1.4290    | -16.99                           | -21.98                           |
| 64.9   | 4.450     | 1.5321    | 4.732     | 1.4251    | -16.94                           | -21.88                           |
| 102.2  | 4.460     | 1.5281    | 4.742     | 1.4215    | -16.81                           | -21.74                           |
| 139.4  | 4.470     | 1.5241    | 4.753     | 1.4177    | -16.60                           | -21.49                           |
| 176.6  | 4.480     | 1.5201    | 4.763     | 1.4142    | -16.55                           | -21.46                           |
| 213.8  | 4.490     | 1.5161    | 4.774     | 1.4104    | -16.49                           | -21.41                           |
| 251.0  | 4.500     | 1.5121    | 4.785     | 1.4066    | -16.27                           | -21.15                           |
| 288.2  | 4.510     | 1.5081    | 4.795     | 1.4031    | -16.13                           | -21.00                           |

These results are very interesting, because when they are converted to actual zero field splittings and added to the mechanisms of chapters one and two (a total of  $\mu=+75.11 \text{ cm}^{-1}$ ), the result is a total splitting which increases initially with temperature. This is in agreement with the data of table 4.1. Unfortunately, this agreement is lost when the results of table 9.2 are added to the total splitting (see the final two columns of the table on the next page). This is a pity, but in view of the uncertainties involved in the calculation, and because the temperature dependencies are very slight, this loss of agreement when all mechanisms are included is perhaps not unexpected. Nevertheless, this calculation does seem to suggest that the actual temperature dependence arises as a result of the action of two competing mechanisms (i.e. the static anharmonic mechanism and the mechanism of the main part of the thesis). The final comparison between experiment and theory is shown in the table on the next page. In this table,  $\Delta E_{\Sigma}$  represents the combined mechanisms of chapters one and two ( $0.421 \text{ cm}^{-1}$ ),  $\Delta E_{eff}$  represents the results of the static anharmonic mechanism, and  $\Delta E_{\Sigma}$  represents the results of table 9.2.

| total zero field splitting as a function of temperature (in cm <sup>-1</sup> ) |                                      |             |                           |   |
|--|--------------------------------------|-------------|---------------------------|---|
| T/K  | Al <sup>3+</sup> with<br>3s-orbitals | 3s-orbitals | 3s-orbitals + 3p-orbitals | 3s-orbitals + 3p-orbitals + 3d-orbitals |
| 27.7   | -0.0028                              | 0.2433      | 0.2946                    | 0.2918                                  |
| 64.9   | -0.0050                              | 0.2456      | 0.2951                    | 0.2901                                  |
| 102.2  | -0.0077                              | 0.2472      | 0.2960                    | 0.2883                                  |
| 139.4  | -0.0103                              | 0.2477      | 0.2973                    | 0.2870                                  |
| 176.6  | -0.0131                              | 0.2467      | 0.2976                    | 0.2845                                  |
| 213.8  | -0.0158                              | 0.2441      | 0.2979                    | 0.2821                                  |
| 251.0  | -0.0185                              | 0.2408      | 0.2993                    | 0.2808                                  |
| 288.2  | -0.0212                              | 0.2353      | 0.3002                    | 0.2790                                  |

In conclusion then, we can say that the introduction of lattice vibrations can lead to important contributions to the zero field splitting, with the temperature dependence appearing to arise as a result of the action of two competing mechanisms, one which dominates at low temperatures, and one which dominates at high temperatures. The main source of error in these calculations is the inexact form chosen for the 3s-orbitals on the oxygen neighbours, and it is this problem which needs to be addressed in any further refinements to the theory.

## APPENDIX A

In this appendix we will give the full expressions for each of the electronic coefficients in equations (6.19) and (6.20). Let us first of all define the following functions:

$$H(m_3) = \langle m_3 | O_a^2 | m_1 \rangle + \langle m_3 | O_b^2 | m_3 \rangle$$

$$H(m_2) = \langle m_1 | O_a^2 | m_1 \rangle + \langle m_2 | O_b^2 | m_2 \rangle$$

The electronic coefficients are then given as follows:

A(r,  $\alpha m_3 \nu$ )

$$= W \langle \alpha, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle m_1 | \nabla_\nu X | \alpha \rangle H(m_3) \quad (1)$$

A(r,  $\alpha m_2 \nu$ )

$$\sum_{m_3} i W \langle \alpha, m_3 | U | m_3, m_1 \rangle \langle m_1 | X | W_m \rangle \langle W_m | \nabla_\mu \nabla_\nu | \alpha \rangle H(m_3) \quad (2)$$

$$= W \langle \alpha, m_3 | U | m_3, m_1 \rangle \langle m_1 | \nabla_\mu | \alpha \rangle \langle W_m | X \nabla_\nu | \alpha \rangle H(m_3) \quad (3)$$

$$+ W \langle \alpha, m_3 | U | m_3, m_1 \rangle \langle m_1 | X \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle H(m_3) \quad (4)$$

$$+ W \langle \alpha, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle m_1 | \nabla_\nu | W_m \rangle \langle W_m | X | \alpha \rangle H(m_3) \quad (5)$$

$$= W \langle \alpha, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle m_1 | X | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle H(m_3) \quad (6)$$

$$= W \langle m_1 | X \nabla_\mu | \alpha \rangle \langle \alpha | \nabla_\nu | W_m \rangle \langle W_m, m_3 | U | m_3, m_1 \rangle H(m_3) \quad (7)$$

$$+ W \langle m_1 | X \nabla_\mu | \alpha \rangle \langle m_3 | \nabla_\nu | W_m \rangle \langle \alpha, W_m | U | m_3, m_1 \rangle H(m_3) \quad (8)$$

$$= W \langle m_1 | X \nabla_\mu | \alpha \rangle \langle W_m | \nabla_\nu | m_3 \rangle \langle \alpha, m_3 | U | W_m, m_1 \rangle H(m_3) \quad (9)$$

$$= W \langle m_1 | X \nabla_\mu | \alpha \rangle \langle W_m | \nabla_\nu | m_1 \rangle \langle \alpha, m_3 | U | m_3, W_m \rangle H(m_3) \quad (10)$$

$$+ W \langle m_1 | X | \alpha \rangle \langle W_m, m_3 | \nabla_{1\mu} U | m_3, m_1 \rangle \langle \alpha | \nabla_\nu | W_m \rangle H(m_3) \quad (11)$$

$$+ W \langle m_1 | X | \alpha \rangle \langle W_m, m_3 | U | m_3, m_1 \rangle \langle \alpha | \nabla_\nu \nabla_\mu | W_m \rangle H(m_3) \quad (12)$$

$$= W \langle m_1 | X | \alpha \rangle \langle \alpha, m_3 | \nabla_{1\mu} U | W_m, m_1 \rangle \langle \alpha | \nabla_\nu | m_3 \rangle H(m_3) \quad (13)$$

$$= W \langle m_1 | X | \alpha \rangle \langle \alpha, m_3 | \nabla_{1\mu} U | m_3, W_m \rangle \langle W_m | \nabla_\nu | m_1 \rangle H(m_3) \quad (14)$$

$$+ W \langle m_1 | X | \alpha \rangle \langle \alpha, W_m | \nabla_{1\mu} U | m_3, m_1 \rangle \langle m_3 | \nabla_\nu | W_m \rangle H(m_3) \quad (15)$$

A(r,  $\alpha m_1 \nu$ )

$$\sum_{m_3} i W \langle \alpha, m_3 | U | m_3, m_1 \rangle \langle m_1 | \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu X | \alpha \rangle H(m_3) \quad (16)$$

$$+ W \langle \alpha, m_3 | U | m_3, m_1 \rangle \langle m_1 | X \nabla_\mu | W_m \rangle \langle W_m | \nabla_\nu | \alpha \rangle H(m_3) \quad (17)$$







$$= \frac{1}{2} \langle \alpha, m_2 | U | m_2, m_2 \rangle \langle m_2 | \nabla_\mu | W_n \rangle \langle W_n | \nabla_\nu | m_1 \rangle \langle m_1, W_n | U | \alpha, W_n \rangle H(m_2) \quad (77)$$

$$+ \frac{1}{2} \langle \alpha, m_2 | U | m_2, m_2 \rangle \langle W_m | \nabla_m | m_1 \rangle \langle W_n | \nabla_n | \alpha \rangle \langle m_1, m_2 | U | W_n, W_m \rangle M(m_2) \quad (78)$$

$$+ \frac{1}{2} \langle \alpha, m_2 | U | m_2, m_1 \rangle \langle m_1 | \nabla_u | W_0 \rangle \langle m_2 | \nabla_v | W_- \rangle \langle W_0, W_- | U | \alpha, m_1 \rangle M(m_2) \quad (79)$$

$$+ \frac{1}{2} \langle m_1 - m_2 | U | \alpha, m_1 \rangle \langle \alpha | \nabla_{+} | W_{+} \rangle \langle W_{+} | \nabla_{-} | W_{-} \rangle \langle W_{-} - m_2 | U | m_2 - m_2 \rangle M(m_2) \quad (A9)$$

$$+ \hbar \langle m_1 - m_2 | [ | \alpha - m_1 \rangle \langle m_5 | \nabla_{-} | W_0 \rangle \langle W_0 | \nabla_{-} | W_{-} \rangle \langle \alpha - W_{-} | ] | m_2 - m_5 \rangle M(m_1) \quad (A.1)$$

$$\mu_1 \leq \mu_2 \Leftrightarrow \mu_1 \leq \mu_2 \text{ (I)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (II)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (III)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (IV)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (V)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (VI)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (VII)} \Leftrightarrow \mu_1 \leq \mu_2 \text{ (VIII)} \quad (8.2)$$

$$M(\alpha) = \frac{1}{2} \left( \frac{1}{\alpha} + \alpha \right) \quad (1.3)$$

$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} dt = \frac{1}{\sqrt{\pi}} \left( \frac{\sqrt{\pi}}{2} \right) = \frac{1}{2}. \quad (9)$$

$$= (m_1, m_2, \dots, m_n) \in \mathbb{N}^n, \text{ such that } m_1 + m_2 + \dots + m_n = n, \text{ and } m_i \geq 0, \text{ for all } i = 1, 2, \dots, n. \quad (34)$$

[illegible]

[illegible]

$$- \langle u_1 | H_{\text{int}} | u_1 \rangle = - \langle u_1 | V_{\mu} | u_1 \rangle + \langle u_1 | V_v | u_1 \rangle = - \langle u_1 | H_{\text{int}} | u_1 \rangle = - \langle u_1 | H_{\text{int}} | u_1 \rangle = - \langle u_1 | H_{\text{int}} | u_1 \rangle \quad (87)$$

$$+ \langle m_1, m_2 | U | \alpha, m_1 \rangle \langle u_\mu | V_\mu | m_2 \rangle \langle u_\nu | V_\nu | m_2 \rangle \langle \alpha, m_2 | U | w_\mu, u_\nu \rangle M(m_2) \quad (88)$$

$$+ \frac{1}{2} \langle m_1, m_2 | U | \alpha, m_1 \rangle \langle \alpha | \nabla_\mu | W_m \rangle \langle m_2 | \nabla_\nu | W_m \rangle \langle W_m, W_m | U | m_2, m_2 \rangle H(m_2) \quad (89)$$

$$+ \frac{1}{2} \langle \alpha | \nabla_y | W_n \rangle \langle W_n, m_2 | U | m_2, m_2 \rangle \langle m_1 | \nabla_y | W_n \rangle \langle W_n, m_2 | U | \alpha, m_1 \rangle = H(m_2) \quad (90)$$

$$+ \frac{1}{2} \langle \alpha | \nabla_{\mu} | W_n \rangle \langle W_n, m_2 | U | m_2, m_2 \rangle \langle m_2 | \nabla_{\nu} | W_n \rangle \langle m_1, W_n | U | \alpha, m_1 \rangle = N(m_2) \quad (91)$$

$$= \frac{1}{2} \langle \alpha | \nabla_{\mu} | W_n \rangle \langle W_n, m_2 | U | m_2, m_2 \rangle \langle W_n | \nabla_{\nu} | \alpha \rangle \langle m_1, m_2 | U | W_n, m_1 \rangle M(m_2) \quad (92)$$

$$= \ln \langle \alpha | \nabla_\mu | W_n \rangle \langle W_n, m_2 | U | m_2, m_2 \rangle \langle W_m | \nabla_\nu | m_1 \rangle \langle m_1, m_2 | U | \alpha, W_m \rangle M(m_2) \quad (93)$$

$$+ \frac{1}{2} \langle m_2 | \nabla_\mu | W_n \rangle \langle \alpha, W_n | U | m_2, m_2 \rangle \langle m_1 | \nabla_\nu | W_n \rangle \langle W_n, m_2 | U | \alpha, m_1 \rangle N(m_2) \quad (94)$$

$$+ \frac{1}{2} \langle m_2 | \nabla_\mu | W_n \rangle \langle \alpha, W_n | U | m_2, m_2 \rangle \langle m_2 | \nabla_\nu | W_n \rangle \langle m_1, W_n | U | \alpha, m_1 \rangle M(m_2) \quad (95)$$

$$= \frac{1}{2} \langle m_2 | \nabla_\mu | W_n \rangle \langle \alpha, W_n | U | m_2, m_1 \rangle \langle W_n | \nabla_\nu | \alpha \rangle \langle m_1, m_2 | U | W_n, m_1 \rangle M(m_2) \quad (96)$$

$$= \frac{1}{2} \langle m_2 | \nabla_\mu | W_2 \rangle \langle \alpha, W_2 | U | m_2, m_1 \rangle \langle W_2 | \nabla_\nu | m_1 \rangle \langle m_1, m_2 | U | \alpha, W_2 \rangle M(m_2) \quad (97)$$

$$= \frac{1}{2} \langle W_n | \nabla_n | m_2 \rangle \langle \alpha, m_2 | U | W_n, m_2 \rangle \langle m_1 | \nabla_n | W_n \rangle \langle W_n, m_2 | U | \alpha, m_1 \rangle M(m_2) \quad (9d)$$

$$= \frac{1}{2} \langle W_0 | \nabla_y | m_2 \rangle \langle \alpha, m_2 | U | W_0, m_1 \rangle \langle m_2 | \nabla_y | W_- \rangle \langle m_1, W_- | U | \alpha, m_1 \rangle H(m_3) \quad (99)$$

$$+ \frac{1}{2} \langle W_{-} | \nabla_{-} | m_2 \rangle \langle \alpha, m_2 | U | W_{-}, m_2 \rangle \langle W_{-} | \nabla_{-} | \alpha \rangle \langle m_1, m_2 | U | W_{-}, m_1 \rangle H(m_2) \quad (100)$$

$$+ \frac{1}{2} \langle \mathbf{M}_1 | \nabla_{\mathbf{r}_1} | m_2 \rangle \langle \alpha, m_2 | || \mathbf{M}_1 - m_2 \rangle \langle \mathbf{M}_1 | \nabla_{\mathbf{r}_1} | m_1 \rangle \langle m_1, m_2 | || \sim \mathbf{M}_1 \rangle \mathbf{M} \langle m_2 \rangle \quad (101)$$

$$- \frac{1}{2} \langle \mathbf{M} | \mathbf{r} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{r} | \mathbf{M} \rangle - \frac{1}{2} \langle \mathbf{M} | \mathbf{r} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{r} | \mathbf{M} \rangle - \frac{1}{2} \langle \mathbf{M} | \mathbf{r} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{r} | \mathbf{M} \rangle - \frac{1}{2} \langle \mathbf{M} | \mathbf{r} | \mathbf{m} \rangle \langle \mathbf{m} | \mathbf{r} | \mathbf{M} \rangle \quad (103)$$

$$- \frac{1}{\pi} \int_0^{2\pi} \ln |m(\theta)| d\theta = \lim_{n \rightarrow \infty} \left( - \frac{1}{\pi} \int_0^{2\pi} \ln |m_n(\theta)| d\theta \right) = M(m) \quad (103)$$

6. 44  $\leq \beta_1 \leq 1.07$   $\Rightarrow$   $\beta_1$  is not a  $\beta$ -value.  $\beta_1 \geq 1.07$   $\Rightarrow$   $\beta_1$  is a  $\beta$ -value.  $\beta_1 \leq 0.44$   $\Rightarrow$   $\beta_1$  is not a  $\beta$ -value.  $\beta_1 \leq 0.44$   $\Rightarrow$   $\beta_1$  is not a  $\beta$ -value.

## APPENDIX B

### Expansion of Off-Site Functions

Most of the matrix elements which we need to evaluate in chapter eight contain, in addition to one or more 4f-orbitals defined with respect to an origin at the centre of the  $Gd^{3+}$  ion, one or more oxygen orbitals defined with respect to an origin at the centre of the appropriate oxygen atom. This arrangement is not especially convenient, and so it is desirable to have all orbitals defined with respect to a single origin. This origin is chosen to be at the centre of the  $Gd^{3+}$  ion, and in this appendix we will discuss the techniques used to rewrite (expand) the oxygen orbitals in terms of displacements from this new origin. Whilst very general methods are available for doing this [Sack 1963; Barnett 1963; Tuszyński and Dixon 1967], they lead to a rather complicated formalism. Since we are only interested in the expansion of s and p-functions, we will consider each case separately.

### B-functions

Consider two sites A and B, and let  $R$  be a vector running from the centre of A to the centre of B. An s-function centred on B takes the form

$$\Psi_s(r_B) = R(r_B) Y_0^0 \quad (B1)$$

For simplicity let us assume that the radial function  $R$  takes the form:

$$R(r_B) = \frac{\lambda}{r_B} \exp[-\lambda r_B] \quad (B2)$$

Suppose now that we want to rewrite this function in terms of coordinates centred on A. Since  $r_A = r_B + R$ , we have

$$\Psi_s(r_A) = R(r_A - R) Y_0^0 \quad (B3)$$

Following Christodoulos et al. (1988), the right hand side of (B3) may be expanded into a series of Legendre polynomials as follows

$$R(|r_A - R|) = \sum_l a_l(\lambda, r_A, R) P_l(\cos \omega) \quad (B4)$$

where the  $P_l$  are Legendre polynomials, and  $\omega$  is the angle between the vectors  $r_A$  and  $R$ . From the orthogonality properties of the Legendre polynomials [Arfken 1970], the coefficients  $a_l(\lambda, r_A, R)$  are found to be

$$a_l(\lambda, r_A, R) = \frac{1}{2} (2l+1) \int_{-1}^1 (1-2hx+h^2)^{1/2} \exp[-AR(1-2hx+h^2)]^{\frac{1}{2}} P_l(x) dx \quad (B5)$$

where  $h=r/R$  and  $x=\cos \omega$ . Christodoulos et al have shown that the evaluation of this integral leads to the following expression:

$$\begin{aligned} a_l(\lambda, r_A, R) = & \frac{(2l+1)R\lambda}{2h} \sum_{q=0}^{[l/2]} \frac{(-1)^q (2l-2q)!}{2^q q! (1-q)! (2h)^{l-2q}} \frac{1-2q}{1-q} \frac{(-1)^q (1+h^2)^{l-2q-q}}{(1-2q-q)! q!} \\ & \times \{ \exp[-AR|h-1|] \sum_{p=0}^{[l+2q]/2} \frac{[h-1]^{l+2q+1-p}}{(AR)^{p+1}} \cdot \frac{(\lambda+2q+1)!}{(\lambda+2q+1-p)!} \\ & - \exp[-AR|h+1|] \sum_{p=0}^{[l+2q+1]/2} \frac{[h+1]^{l+2q+1-p}}{(AR)^{p+1}} \cdot \frac{(\lambda+2q+1)!}{(\lambda+2q+1-p)!} \} \quad (B6) \end{aligned}$$

In this expression,  $[l/2]$  denotes the integer part of  $l/2$ .

In (B4) it is convenient to reexpress the Legendre polynomials in terms of spherical harmonics using the addition theorem [Edmonds 1950]:

$$P_l(\cos \omega) = \sum_m \lambda(l) Y_l^m(\theta_R, \phi_R) Y_l^m(\theta_A, \phi_A) \quad (B7)$$

where  $\theta_R$  and  $\phi_R$  define the orientation of the vector  $R$  with respect to coordinates centred on  $A$ , and  $\lambda(l) = 4\pi/(2l+1)$ . (B3) then becomes

$$\Psi_A(r_A) = \sum_{lm} \lambda(l) a_l(\lambda, r_A, R) Y_l^m(r_A) Y_l^m(\theta_A, \phi_A) \quad (B8)$$

where we have written  $R$  and  $A$  for the variables  $\theta_R, \phi_R$  and  $\theta_A, \phi_A$  respectively.

## P-Functions

The expansion of a p-functions is very similar to that of an s-function, except that this time we have to consider

$$\Psi_p(r_B) = R(r_B) Y_l^m(\theta_B, \phi_B) \quad (B9)$$

Again we will assume that  $R(r_B)$  is a Slater orbital of the form (B2). On moving to a set of coordinates centred at A, the radial part of (B9) is treated in exactly the same way as that for an s-function. To see what happens to the spherical harmonic, it is easiest to work in Cartesian coordinates. Since  $r_B = r_A - R$ , we easily find that

$$Y_l^m(\theta_B, \phi_B) = 1/|r_A - R| [r_A Y_l^m(\theta_A, \phi_A) - R Y_l^m(\theta_A, \phi_R)] \quad (B10)$$

Therefore, using (B10) and (B4), (B9) becomes

$$\Psi_p(r_A) = \sum_l a_l(\lambda-1, r_A, R) P_l(\cos \omega) [r_A Y_l^m(A) - R Y_l^m(R)] \quad (B11)$$

where the coefficient  $a_l(\lambda-1, r_A, R)$  is given by (B5). With the help of (B7), (B11) finally becomes

$$\Psi_p(r_A) = \sum_{lm} a_l(\lambda-1, r_A, R) Y_l^m(R) Y_l^m(A) [r_A Y_l^m(A) - R Y_l^m(R)] \quad (B12)$$

Equations (B8) and (B12) are the final expressions which we seek. Note that the generalization of (B8) and (B12) to the cases where  $R(r_B)$  is a linear combination of Slater orbitals is perfectly straightforward.

# APPENDIX C

In table C1 we list the symmetrized basis vectors  $\{g\}$  for the  $C_{3h}$  symmetry group obtained from the Cartesian basis vectors  $\{x\}$ .

| Table C1: symmetrized basis $\{g\}$ in terms of Cartesian basis $\{x\}$ |               |   |
|---|---------------|---|
| IRR   | $\sigma$      | basis vectors: ( with $a\sigma/3/2$ $b\sigma/2$ )                   |
| A'  | $\sigma_1$    | $(-bx_1+ay_1-bx_2-ay_2+bx_3+ay_3-bx_4-ay_4+bx_5+ay_5)/\sqrt{6}$     |
|   | $\sigma_2$    | $(ax_1+by_1-ax_2+by_2-ax_3+by_3-ax_4+by_4-ax_5+by_5)/\sqrt{6}$      |
|   | $\sigma_3$    | $(z_1+z_2+z_3-z_4-z_5)/\sqrt{6}$                                    |
|   | $\sigma_4$    | $(bx_4+ay_4-x_5+bx_5-ay_5)/\sqrt{3}$                                |
|   | $\sigma_5$    | $(ax_4-by_4+y_5-ax_5-by_5)/\sqrt{3}$                                |
| A''   | $\sigma_6$    | $(-bx_1+ay_1-bx_2-ay_2+bx_3+ay_3-bx_4-ay_4+bx_5+ay_5-x_6)/\sqrt{6}$ |
|   | $\sigma_7$    | $(ax_1+by_1-ax_2+by_2-ax_3+by_3-ax_4+by_4-ax_5+by_5-y_6)/\sqrt{6}$  |
|   | $\sigma_8$    | $(z_1+z_2+z_3+z_4+z_5)/\sqrt{6}$                                    |
|   | $\sigma_9$    | $(z_4+z_5+z_6)/\sqrt{6}$  |
| E'  | $\sigma_{10}$ | $(-x_1+2ay_1+bx_2+ay_2-x_3-x_7+2ay_7+bx_8+ay_8-x_9)/\sqrt{12}$      |
|   | $\sigma_{11}$ | $(2ax_1+y_1+ax_2-by_2+y_3+2ax_7+y_7+ax_8-by_8+y_9)/\sqrt{12}$       |
|   | $\sigma_{12}$ | $(2z_1-z_2-z_3-2z_7-z_8-z_9)/\sqrt{12}$                             |
|   | $\sigma_{13}$ | $(-bx_3-ay_3-x_4-bx_4-ay_4-x_5)/2$                                  |
|   | $\sigma_{14}$ | $(-ax_3+by_3+y_4-ax_4+by_4+y_5)/2$                                  |
|   | $\sigma_{15}$ | $(z_2-z_3-z_4+z_5)/2$   |
|   | $\sigma_{16}$ | $(x_4+2ay_4+x_5-by_5+ay_5)/\sqrt{6}$                                |
|   | $\sigma_{17}$ | $(-x_5-by_5+ay_5)/\sqrt{2}$   |
|   | $\sigma_{18}$ | $(2ax_4-y_4-y_5+ax_5+by_5)/\sqrt{6}$                                |
| E''   | $\sigma_{19}$ | $(y_5+ax_5+by_5)/\sqrt{2}$  |
|   | $\sigma_{20}$ | $(-x_1+2ay_1+bx_2+ay_2-x_3-x_7-2ay_7-bx_8-ay_8+x_9)/\sqrt{12}$      |
|   | $\sigma_{21}$ | $(2ax_1+y_1+ax_2-by_2+y_3-2ax_7-y_7-ax_8+by_8-y_9)/\sqrt{12}$       |
|   | $\sigma_{22}$ | $(2z_1-z_2-z_3+2z_7+z_8+z_9)/\sqrt{12}$                             |
|   | $\sigma_{23}$ | $(-bx_2-ay_2-x_3+bx_3+ay_3+x_9)/2$                                  |
|   | $\sigma_{24}$ | $(-ax_2+by_2+y_3+ax_3-by_3-y_9)/2$                                  |
|   | $\sigma_{25}$ | $(z_2-z_3+z_8-z_9)/2$   |
|   | $\sigma_{26}$ | $(2z_4-z_5-z_6)/\sqrt{6}$   |
|   | $\sigma_{27}$ | $(z_6-z_9)/\sqrt{2}$  |

In tables C2 to C5 we give the four blocks of the transformed force matrix  $K'$ , corresponding to the four irreducible representations of  $C_{3h}$ . Each element is multiplied by a factor  $k/M$ .

|        |        |        |       |       |
|--------|--------|--------|-------|-------|
| 0.453  | -0.012 | 0.447  | 0.000 | 0.000 |
| -0.012 | 0.101  | -0.012 | 0.000 | 0.000 |
| 0.447  | -0.012 | 0.646  | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 1.100 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |

Table C2:

(for  $A'$  IRREP)

|        |        |        |       |
|--------|--------|--------|-------|
| 0.453  | -0.012 | 0.447  | 0.000 |
| -0.012 | 0.101  | -0.012 | 0.000 |
| 0.447  | -0.012 | 0.646  | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000 |

Table C3:

(for  $A''$  IRREP)

Table C4: (for  $E'$  IRREP)

|        |        |        |        |        |        |       |       |       |       |
|--------|--------|--------|--------|--------|--------|-------|-------|-------|-------|
| 0.453  | -0.012 | 0.447  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 | 0.000 | 0.000 |
| -0.012 | 0.101  | -0.012 | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.447  | -0.012 | 0.646  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.453  | -0.012 | 0.447  | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | -0.012 | 0.101  | -0.012 | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.447  | -0.012 | 0.646  | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 1.100 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000 | 1.100 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 | 0.000 | 0.000 |

|        |        |        |        |        |        |       |       |
|--------|--------|--------|--------|--------|--------|-------|-------|
| 0.453  | -0.012 | 0.447  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |
| -0.012 | 0.101  | -0.012 | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |
| 0.447  | -0.012 | 0.646  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.453  | -0.012 | 0.447  | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | -0.012 | 0.101  | -0.012 | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.447  | -0.012 | 0.646  | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |
| 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000  | 0.000 | 0.000 |

Table C5:

(for  $E''$   
IRREP)



## APPENDIX D

### Wannier Functions

In the Method of Stevens, extensive use is made of second quantization techniques, because they provide a useful bridge between the Slater determinant formalism of the many-electron problem and the angular momentum formalism of the effective operator  $H_{eff}$ . In order to use the second quantization techniques, one requires a complete, orthonormal set of basis functions. The second quantized operators are defined with reference to this set of basis functions. In a magnetic insulator one would expect that the basis functions should be well localized about the atomic sites in the lattice. Atomic functions will not do for this purpose, because they do not satisfy the completeness and orthonormality requirements. Instead, one can use Wannier functions. To begin, let us assume that the band structure of the crystal is known, so that we have a set of band wavefunctions:

$$\Psi_k(r) = U_{nk}(r) \exp[ik \cdot r] \quad (D1)$$

The Wannier functions are then constructed as follows [Harrison 1980]:

$$W_n(r-r_j) = N^{-1} \sum_k U_{nk}(r) \exp[ik \cdot (r-r_j)] \quad (D2)$$

In this expression  $k$  refers to the  $k$ -vectors belonging to the first Brillouin zone, and  $n$  is the band index. These Wannier functions may be shown to have the following properties:

- 1) The Wannier function  $W_n(r-r_j)$  is localized about the site  $r_j$  in the lattice.
- 2) The Wannier function  $W_n(r-r_j)$  is orthogonal to the Wannier function  $W_m(r-r_l)$ , if  $m \neq n$  or  $j \neq l$  (or of course both).

The definition (D2) depends on the crystal lattice being periodic. If the lattice is not periodic, then one is faced with a much more complicated problem if one wants to define sets of localized functions centred on the lattice points. Such cases arise if, for instance, the crystal is finite,

or if it contains defects. Attempts have been made to deal with these cases, the analogous functions being known as 'Generalized Wannier Functions' [Kohn and Offroy 1973].

# APPENDIX E

In this appendix we will tabulate the contributions which the individual terms in appendix A make to the coefficients  $A(j)$  and  $C(j)$ , when they are substituted into equations (6.19) and (6.20). From the approximations and assumptions which were made in chapter eight, we can immediately ignore all of the following terms from appendix A:

(8), (10), (14), (15), (19), (21), (26), (28), (30), (32), (34), (36)  
 (37), (38), (40), (41), (42), (48), (50), (52), (54), (56), (60), (63)  
 (65), (67), (71), (73), (74), (75), (77), (78), (79), (81), (83), (84)  
 (85), (87), (88), (89), (91), (93), (94)-(97), (99), (101), (102)-(105)  
 (46), (81), (69), (76)

The following tables contain the contributions of the terms which remain as functions of the normal coordinate index  $j$ . All values are in units of  $(a^2/a_0)^2 \cdot (1/a_0)^2$ .

| Table E1: contributions from terms in appendix A ( $\times 10^{-5}$ ), $j=1$ to 11 |     |     |       |      |     |     |       |     |     |      |      |
|--|-----|-----|-------|------|-----|-----|-------|-----|-----|------|------|
| term   | j=1 | j=2 | j=3   | j=4  | j=5 | j=6 | j=7   | j=8 | j=9 | j=10 | j=11 |
| 1  | -10 | -4  | -2364 | 3063 | -10 | -4  | -2364 | -10 | -9  | -3   | -3   |
| 2  | 14  | 15  | 15    | -18  | 14  | 15  | 15    | 14  | 15  | 14   | 15   |
| 3  | 5   | 9   | 363   | -465 | 5   | 9   | 363   | -12 | 26  | 13   | 4    |
| 4  | -6  | -3  | 105   | -132 | -6  | -3  | 105   | -6  | -5  | -3   | -3   |
| 5  | 2   | 0   | -12   | 4    | 2   | 0   | -12   | 2   | 2   | 0    | 0    |
| 6  | -2  | -4  | -4    | -42  | -2  | -4  | -4    | -2  | -2  | -4   | -4   |
| 7  | 0   | 0   | 0     | 0    | 0   | 0   | 0     | 0   | 0   | 0    | 0    |
| 9  | 4   | -2  | -562  | -358 | 4   | -2  | -562  | 5   | 2   | 0    | -2   |
| 11   | 0   | 0   | 0     | 0    | 0   | 0   | 0     | 0   | 0   | 0    | 0    |
| 12   | 19  | 20  | 20    | -26  | 19  | 20  | 20    | 19  | 20  | 19   | 20   |
| 13   | 1   | 0   | 0     | 0    | 1   | 0   | 0     | 1   | 2   | 0    | 0    |
| 16   | -6  | -4  | 93    | -18  | -6  | -4  | 93    | -6  | -5  | -4   | -4   |
| 17   | -6  | -3  | 105   | -132 | -6  | -3  | 105   | -6  | -5  | -3   | -3   |
| 18   | 0   | 0   | 0     | 0    | 0   | 0   | 0     | 0   | 0   | 0    | 0    |
| 20   | 0   | 0   | 0     | 0    | 22  | 0   | 0     | -1  | -2  | 0    | 0    |

|     |    |    |     |      |    |    |     |    |    |    |    |
|-----|----|----|-----|------|----|----|-----|----|----|----|----|
| 22  | -1 | -1 | -62 | 80   | -1 | -1 | -62 | -1 | -1 | -1 | -1 |
| 23  | 0  | 0  | -12 | 15   | 0  | 0  | -12 | 0  | -1 | 0  | 0  |
| 24  | -1 | 0  | -2  | 0    | -1 | 0  | -2  | 0  | -3 | -1 | 1  |
| 25  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 27  | -2 | 0  | -16 | 20   | -2 | 0  | -16 | -2 | -2 | 0  | 0  |
| 29  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 31  | 4  | 0  | 4   | -54  | 4  | 0  | 4   | 4  | 4  | 0  | 0  |
| 33  | 1  | 0  | 2   | 0    | 1  | 0  | 2   | 0  | 2  | 1  | 0  |
| 35  | 4  | 0  | 32  | 0    | 4  | 0  | 32  | 4  | 2  | 0  | 0  |
| 39  | 4  | 0  | 34  | 0    | 4  | 0  | 34  | 4  | 2  | 0  | 0  |
| 43  | 3  | 1  | 89  | -116 | 3  | 1  | 89  | 3  | 3  | 1  | 1  |
| 44  | 1  | 1  | 1   | -7   | 1  | 1  | 1   | 1  | 1  | 1  | 1  |
| 45* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 47  | 0  | 0  | 2   | 2    | 0  | 0  | 2   | 0  | 0  | 0  | 0  |
| 49  | -2 | 0  | 72  | -94  | -2 | 0  | 72  | -2 | -2 | 0  | 0  |
| 51* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 53* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 55  | -3 | -1 | 66  | -87  | -4 | -1 | 66  | -6 | -4 | -1 | -1 |
| 57* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 58  | -3 | -3 | -3  | -5   | -3 | -3 | -3  | -3 | -3 | -3 | -3 |
| 59  | -5 | 0  | -7  | 0    | -5 | 0  | -7  | -3 | -9 | 0  | 0  |
| 62* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 64  | 6  | 0  | 9   | 63   | 6  | 0  | 9   | 3  | 9  | 0  | 0  |
| 66  | 0  | 0  | -2  | -2   | 0  | 0  | -2  | 0  | 0  | 0  | 0  |
| 68* | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 70  | 0  | 0  | -2  | 1    | 0  | 0  | -2  | 1  | 0  | 0  | 0  |
| 72  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 80  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 82  | -2 | 0  | 5   | -22  | -2 | 0  | 5   | -3 | -1 | 0  | 0  |
| 86  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 90  | 0  | 0  | 1   | -11  | 0  | 0  | 1   | 0  | 0  | 0  | 0  |
| 92  | 0  | 0  | 0   | 0    | 0  | 0  | 0   | 0  | 0  | 0  | 0  |
| 98  | 8  | 0  | 74  | -96  | 8  | 0  | 74  | 8  | 8  | 0  | 0  |
| 100 | 2  | 0  | -11 | 30   | 2  | 0  | -11 | 1  | 4  | -2 | 1  |

Table E1 (ccnt.): contribution (x 10<sup>-5</sup>) j=12 to 21

| term | j=12  | j=13  | j=14 | j=15 | j=16 | j=17 | j=18 | j=19 | j=20  | j=21  |
|------|-------|-------|------|------|------|------|------|------|-------|-------|
| 1    | -2348 | -2323 | 3057 | 3044 | -10  | -9   | -3   | -3   | -2348 | -2323 |
| 2    | 15    | 15    | -18  | -18  | 14   | 15   | 14   | 15   | 15    | 15    |
| 3    | 368   | 333   | -583 | -343 | -12  | 26   | 13   | 4    | 368   | 333   |
| 4    | 105   | 105   | -132 | -132 | -6   | -5   | -3   | -3   | 105   | 104   |
| 5    | -12   | -11   | 4    | 3    | 2    | 2    | 0    | 0    | -12   | -11   |
| 6    | -4    | -4    | -42  | -42  | -2   | -2   | -4   | -4   | -4    | -4    |
| 7    | -21   | 21    | 43   | -43  | 0    | 0    | 0    | 0    | -21   | 21    |
| 9    | -705  | -409  | -446 | -265 | 5    | 2    | 0    | -2   | -705  | -409  |
| 11   | 2     | -2    | -3   | 3    | 0    | 0    | 0    | 0    | 2     | -2    |
| 12   | 20    | 19    | -26  | -26  | 19   | 20   | 19   | 20   | 20    | 19    |
| 13   | 0     | 0     | 0    | 0    | 1    | 2    | 0    | 0    | 0     | 0     |
| 16   | 94    | 93    | -118 | -118 | -6   | -5   | -4   | -4   | 94    | 93    |
| 17   | 105   | 105   | -132 | -132 | -6   | -5   | -3   | -3   | 105   | 104   |
| 18   | 2     | -2    | -3   | 3    | 0    | 0    | 0    | 0    | 2     | -2    |
| 20   | -1    | 0     | 28   | 26   | -1   | -2   | 0    | 0    | -1    | 0     |
| 22   | -62   | -62   | 80   | 80   | -1   | -1   | -1   | -1   | -62   | -62   |
| 23   | -12   | -11   | 18   | 12   | 0    | -1   | 0    | 0    | -12   | -11   |
| 24   | -2    | -4    | -1   | 1    | 0    | -3   | -1   | 1    | -2    | -4    |
| 25   | 0     | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0     |
| 27   | -16   | -16   | 20   | 20   | -2   | -2   | 0    | 0    | -16   | -16   |
| 29   | 0     | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0     |
| 31   | 4     | 4     | -54  | -54  | 4    | 4    | 0    | 0    | 4     | 4     |
| 33   | 2     | 2     | 0    | 0    | 0    | 2    | 1    | 0    | 2     | 2     |
| 35   | 28    | 36    | 16   | -16  | 4    | 2    | 0    | 0    | 28    | 36    |
| 39   | 28    | 36    | 16   | -16  | 4    | 2    | 0    | 0    | 28    | 36    |
| 43   | 89    | 88    | -116 | -116 | 3    | 3    | 1    | 1    | 89    | 88    |
| 44   | 1     | 1     | -7   | -7   | 1    | 1    | 1    | 1    | 1     | 1     |
| 45   | 0     | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0     |
| 47   | 0     | 2     | 2    | 2    | 0    | 0    | 0    | 0    | 0     | 2     |
| 49   | 72    | 70    | -94  | -94  | -2   | -2   | 0    | 0    | 72    | 70    |
| 51   | 0     | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0     |
| 53   | 0     | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0     | 0     |
| 55   | 67    | 65    | -93  | -80  | -6   | -4   | -1   | -1   | 67    | 65    |

|     |     |     |      |     |    |    |    |    |     |     |
|-----|-----|-----|------|-----|----|----|----|----|-----|-----|
| 57* | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 58  | -3  | -3  | -5   | -5  | -3 | -3 | -3 | -3 | -3  | -3  |
| 59  | -4  | -11 | 0    | 0   | -3 | -9 | 0  | 0  | -4  | -11 |
| 62* | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 64  | 5   | 12  | 29   | 17  | 3  | 9  | 0  | 0  | 5   | 12  |
| 66  | 0   | -2  | -2   | -2  | 0  | 0  | 0  | 0  | 0   | -2  |
| 68* | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 70  | -2  | -2  | 1    | 1   | -1 | 0  | 0  | 0  | -2  | -2  |
| 72  | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 76  | 2   | 1   | -10  | -6  | -2 | -1 | 0  | 0  | 2   | 1   |
| 80  | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 82  | 4   | 8   | -32  | -11 | -3 | -1 | 0  | 0  | 4   | 6   |
| 86  | -1  | 1   | -3   | 4   | 0  | 0  | 0  | 0  | -1  | 1   |
| 92  | 0   | 0   | 0    | 0   | 0  | 0  | 0  | 0  | 0   | 0   |
| 98  | 76  | 70  | -104 | -86 | 8  | 8  | 0  | 0  | 76  | 70  |
| 100 | -21 | 0   | 21   | 40  | 1  | 4  | -2 | 1  | -21 | 0   |

Some of the terms in these tables are marked with an asterisk (\*). It is found that these terms do not make any real contribution to the  $A(j)$  or  $C(j)$  coefficients. However it is found that the contributions corresponding to the degenerate normal coordinate pairs  $(j=8,9), (j=10,11), (j=12,13), (j=14,15), (j=16,17), (j=18,19), (j=20,21)$  are pure imaginary, and the contribution from one member of a pair is the complex conjugate of the other member. When added together, these contributions cancel one another, and thus  $A(j)$  and  $C(j)$  remain real numbers.

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